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FINAL REPORT on PHASE I

ATMOSPHERIC REACTION STUDIES IN THE LOS ANGELES BASIN

VOLUME I

Prepared for

COORDINATING RESEARCH COUNCIL, INC.

NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

(Contract No. CPA 22-69-19)

Prepared by

SCOTT RESEARCH LABORATORIES, INC.
P. O. BOX D-11
PLUMSTEADVILLE, PENNSYLVANIA 18949

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The pollutants measured included carbon monoxide, oxidant, ozone, nitric oxide, nitrogen dioxide, total hydrocarbons, individual C_1 to C_{10} hydrocarbons, peroxyacetyl nitrate, formaldehyde, acrolein and total aliphatic aldehydes. The meteorological elements monitored included temperature, relative humidity, wind speed and direction, and ultraviolet radiation intensity. The most significant advance was the chromatographic determination of more than 100 individual hydrocarbons.

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Total Hydrocarbons
Flame Ionization
Acrolein
Total Aliphatic Aldehydes
Tedlar Bags
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on Phase I of

Atmospheric Reaction Studies
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APRAC Project CAPA 7-68

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SUMMARY

A comprehensive survey of the atmosphere of the Los Angeles Basin was conducted during the period August 22 to November 14, 1968. A large number of contaminants were determined continuously and periodically, and readings of pertinent meteorological factors were made at two ground level sites and in an aircraft at several altitudes above the ground sites.

Two 8' x 35' mobile trailer-type laboratories were fabricated specifically for use in this study. The trailers contain instrumentation for continuous monitoring of a number of contaminants, photochemical products and meteorological parameters. They also contain chromatographs and wet chemical apparatus to determine a large number of additional pollutants periodically.

The pollutants measured included carbon monoxide, oxidant, ozone, nitric oxide, nitrogen dioxide, total hydrocarbons, individual C_1 to C_{10} hydrocarbons, peroxyacetyl nitrate, formaldehyde, acrolein and total aliphatic aldehydes. The meteorological elements monitored included temperature, relative humidity, wind speed and direction, and ultraviolet radiation intensity. The most significant advance in the analytical art was the chromatographic determination of more than 100 individual hydrocarbons from C_5 to C_{10} with a sensitivity in the tenth of a part per billion range by the use of a capillary column with on-column freeze-out.

A Waco Model 220-S aircraft was equipped to measure air temperature, relative humidity, oxidant, and both incoming and outgoing ultraviolet irradiation. Facilities to sample oxides of nitrogen in bubblers and carbon monoxide and hydrocarbons in Tedlar bags were also included.

The trailers were located in Huntington Park and at El Monte airport. These two sites were 12.7 miles apart along a prevailing air trajectory. The airport site facilitated transfer of airborne samples. Periodic sampling and analysis was performed during the time of day which normally included contaminant buildup and maximum oxidant formation. Aircraft flights were scheduled for morning and afternoon on days of moderate to heavy smog. Vertical profiles were recorded over each ground site and samples were collected at specific altitudes within the inversion layer. Special investigations of smog fronts were made on several occasions.

A total of nearly 100,000 data points was reduced and tabulated. These included half-hourly averages for elements measured continuously on the ground and values at altitude increments of 100 feet for the airborne measurements.

The in-depth analysis of the massive volume of data collected, performed as Phase II of the program, must be completed before concise statements regarding the photochemical system in the Los Angeles Basin can be made. The complexity of the system is amply illustrated and the need to study air parcels on a real time basis is pointed out.

The individual elements are discussed through graphic illustrations of diurnal patterns for five selected days centered around the major smog episode encountered in the study. A brief explanation is given of the pattern for each of the five days based on visual inspection of the data. The transport of contaminants from the Huntington Park area to El Monte and the resulting enhancement of oxidant production is well documented. The persistence of high oxidant levels after contaminant

concentrations had been greatly reduced by dilution is of interest as are the high oxidant levels found aloft at heights where hydrocarbon and nitrogen oxide concentrations were extremely low.

The availability, for the first time, of gas chromatographic data for more than 100 individual hydrocarbons covering the complete range present in a polluted atmosphere offers a means of gaining much additional insight into the sources of pollutants, relative source strength, the rates of photochemical reactions and the extent to which they have proceeded. This information will be developed in the data analysis (Phase II).

1. INTRODUCTION

This report describes the work performed by Scott Research Laboratories, Inc. and its sub-contractor Bolt, Beranek and Newman, Inc. on APRAC Project No. CAPA-7-68, "Atmospheric Reaction Studies in the Los Angeles Basin" (Contract No. CPA-22-69-19). This project was sponsored jointly by the National Air Pollution Control Administration and the Coordinating Research Council, Inc.

This report is contained in two volumes. Volume I includes a complete description of the study methodology as well as a thorough representation of the quantitative and qualitative results obtained. Volume II displays all of the relevant raw data which were collected in the test operations and processed by manual or machine techniques.

1.1 PREVIOUS STUDIES

A large number of atmospheric measurements have been made in the Los Angeles Basin during the last 15 years. A comprehensive study of air pollution in the Los Angeles Basin was conducted in 1954. The instrumentation available at that time was quite inferior to that currently in use. The California State Department of Health has been collecting data in its various counties for a period of years, and the Los Angeles County Air Pollution Control District has also operated a group of monitoring stations for an extended period. A number of specialized studies have been conducted during the last several years which involved intercomparisons of measurements by different methods at one or two sites. The work was frequently limited to a single type of pollutant such as oxidants, hydrocarbons or carbon monoxide. Similar comparative measurements were

made of ultraviolet radiation measurement techniques. Dr. E. R. Stephens of UCR has determined the composition of light hydrocarbons in a number of samples collected at various locations in the Los Angeles Basin and other sections of California. The Division of Chemical and Physical Research and Development of NAPCA collected comprehensive data in downtown Los Angeles and Azusa during the fall of 1967 and 1968.

Except for the recent NAPCA work, all of the studies have failed to provide comprehensive, concurrent data for the wide range of chemical and meteorological factors which affect photochemical smog formation. Therefore, their usefulness in explaining the behavior of the Basin atmosphere is quite limited.

A great number of laboratory irradiation chamber studies have been performed on synthetic hydrocarbon - nitrogen oxide mixtures and on diluted auto exhaust. The results obtained by different investigators have often been contradictory especially in predicting the effects of suggested control measures such as nitrogen oxide reduction and lower fuel volatility. It is not unreasonable to believe that ambiguities should arise since the laboratory systems usually bear little resemblance to the atmosphere. We must, therefore, resort to atmospheric reaction studies to resolve these ambiguities and to develop a meaningful course of action to alleviate the manifestations of photochemical smog.

1.2 LONG RANGE OBJECTIVES

The ultimate objective of these studies is to develop a working model of the Los Angeles Basin atmosphere which can be used to define the qualitative and quantitative aspects of photochemical smog. With this

model it would be possible to predict the behavior of the system from day to day at various locations in the Basin, to designate the relative contribution of various contaminants and sources to photochemical smog, and to evaluate the effectiveness of possible control measures in reducing smog manifestations. It should also be possible to follow the changes in contaminant concentrations from year to year and to project the smog levels for future years.

1.3 OBJECTIVES OF 1968 PROGRAM

In keeping with the long range goals of the program, the objectives of the 1968 program were as follows:

1. Acquire and equip two mobile laboratories and an aircraft capable of measuring a large number of chemical and meteorological parameters associated with the formation of photochemical smog.

2. Set up the mobile laboratories at two sites along reasonable air trajectories into the Azusa area.

3. Make continuous and periodic measurements of the various parameters at the two ground sites during the period from August 22 to November 15, 1968.

4. Make airborne measurements of as many parameters as practical in the vertical plane above the ground sites on approximately 15 selected days.

5. Reduce and tabulate the collected data and present it in a form suitable for further analysis and interpretation.

1.4 OUTLINE OF REPORT

Volume I of this report has been organized into six sections following the introduction.

Section 2 describes the equipment and methodology used in conducting the study.

Section 3 discusses the program design and test operations.

Section 4 itemizes the data file collected during test operations.

Section 5 provides an explanation of the data and gives graphical illustrations of typical diurnal patterns.

The report concludes with acknowledgements and references in Sections 6 and 7.

2. EQUIPMENT AND PROCEDURES

2.1 MOBILE LABORATORIES

Two identical mobile trailer-type laboratories were fabricated specially for use in the Los Angeles Basin Survey. A view of the exterior of one of the trailers is shown in Figure 2-1. One trailer was supplied as part of the contract and became government-owned property while the second remained Scott property. The customer (government-owned) trailer contains instrumentation for continuous monitoring of several contaminants, for periodic sampling and analysis of additional contaminants and photochemical products, and for monitoring of meteorological factors. The Scott trailer contains the same instrumentation as the customer trailer except that it does not have the continuous monitoring instruments. Several views of the interior of the customer trailer are shown in Figure 2-2. A summary of the instrumentation contained in the trailers is given in Table 2-1.

The trailers were constructed by Mar-Val Industries, Inc. of Exeter, Pa. to Scott specifications. The instrumentation, sampling manifold and accessories were installed in Scott's San Bernardino Laboratory. The mobile units are 8' x 35' with two exterior doors and one thermopane window. The exterior is aluminum, and the interior is birch paneling. Temperature control is provided by a Westinghouse heat pump with air conditioner. The units are equipped with a self-contained water system, water pump, septic tank, hot water heater and marine toilet. Power is provided through a 200 ampere, 220 volt entrance and distribution panel. Each instrument has its own circuit from the main panel.

A schematic of the interior of the trailer, showing the arrangement

Table 2-1 Trailer Instrumentation

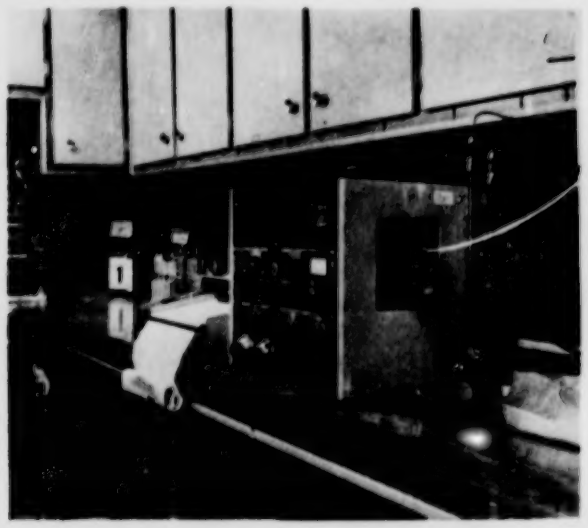
Instrument	Parameter Measured
Beckman Model 315 AL Infrared Analyzer*	Carbon Monoxide
Beckman Model 108A Total Hydrocarbon Analyzer*	Total Hydrocarbons
Beckman Model K-78 Acralyzer***	Oxidant
Beckman Model K-75 Acralyzer***	Nitric Oxide, Nitrogen Dioxide
Mast Model 724-2 Ozone Recorder with Olefin Titration Apparatus	Oxidant, Ozone
Perkin-Elmer Model 900 Gas Chromatograph Infotronics Model CRS-100 Integrator-Printer	Individual C_1 to C_{10} Hydrocarbons
Varian Aerograph Model 1532-2B Gas Chromatograph with Helium Ionization Detectors**	Carbon Monoxide
Varian Aerograph Hy-Fi Model 1220-1 Gas Chromatograph with Electron Capture Detector	Peroxyacetyl Nitrate
BBN Gas Sampler Bausch and Lomb Spectronic 20	Nitric Oxide, Nitrogen Dioxide, Formaldehyde, Acrolein, Aliphatic Aldehydes
Climet Wind Set	Wind Speed and Direction
Bendix Hygro-thermograph	Temperature, Relative Humidity
Eppley Radiation Photometer	Solar UV Radiation Intensity

* Customer trailer only
** Scott trailer only
*** Received after completion of program (Customer trailer only)

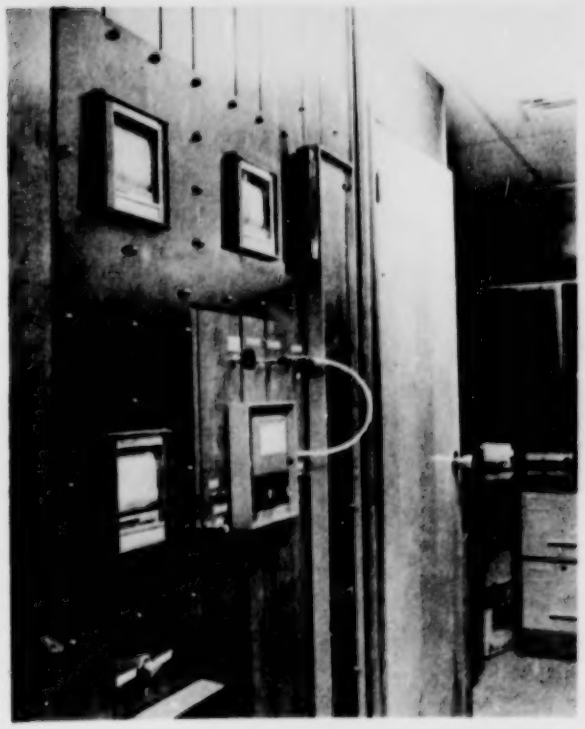
Figure 2-1 Air Monitoring Laboratory Located at El Monte, California

Figure 2-2 Instrumentation in Air Monitoring Laboratory Located at Huntington Park, California

Gas Chromatograph, Integrator-Digitizer, Recorder and Printer-Tape Punch for Individual Hydrocarbons



Bubblers for NO, NO_2, Aldehydes, etc. (background). Gas Chromatograph and Recorder for PAN (foreground)



Long-path Infrared Analyzer for CO. FID for Total Hydrocarbon (tip of case showing) and Recorders for CO, HC, Oxidant, NO and NO_2

Colorimeter and Facilities for Wet Chemistry. Chromatograph for PAN (extreme right)

of instrumentation, counters, desks and sink is shown in Figure 2-3. Storage space is provided under the desk and counters as well as in the overhead cabinets.

The mast for the wind instruments, the hygro-thermograph and the solar UV radiation sensor were mounted on top of the building containing the trailer at Huntington Park. At El Monte these sensors were mounted on the roof of the trailer.

The sampling manifold was constructed of four-foot lengths of one-inch OD Pyrex tubing supplied by Ace Glass Company. The individual sections are connected in such a manner that the air being sampled comes in contact only with Pyrex. The air was sampled through an inverted cone located approximately four feet above the roof. A commercial vacuum cleaner, placed at the system outlet, is used to draw air rapidly through the sampling manifold.

2.2 INSTRUMENTATION AND PROCEDURES FOR CHEMICAL ANALYSIS

2.2.1 Carbon Monoxide

Carbon monoxide was measured continuously with a Beckman Model 315AL Infrared Analyzer with a nominal range of 0 to 50 ppm. The analyzer contains an optical filter to eliminate interference from atmospheric moisture. The instrument was calibrated daily using Scott "Close Tolerance" Analyzed Gas Mixtures.

The Scott trailer contained an Aerograph Model 1532-2B Chromatograph with dual helium ionization detectors. This instrument was used to measure carbon monoxide at ground level and in airborne samples which were collected in Tedlar bags. The carbon monoxide was separated with a 1/8 inch x 10 foot column of Type 5A Molecular Sieve operated at 70°C.

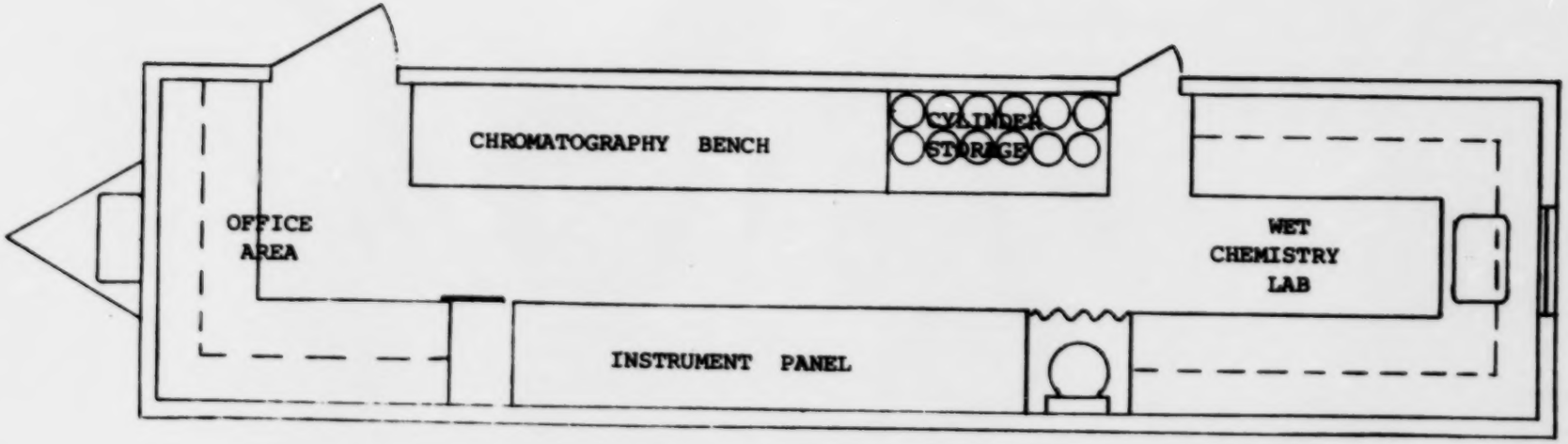


Figure 2-3 Mobile Laboratory Layout

2.2.2 Oxidants and Ozone

In both trailers oxidants and ozone were monitored with Mast Ozone Recorders equipped with olefin titration apparatus[1]. Ozone was determined primarily during periods of elevated oxidant values. During these periods ozone and oxidant were monitored in alternate 7 minute cycles. The Beckman Model K-78 Acralyzer for oxidants was not delivered until after the completion of the field sampling program.

2.2.3 Nitric Oxide and Nitrogen Dioxide

Nitric oxide and nitrogen dioxide were determined using a modified Saltzman procedure. The samples were collected and analyzed manually because the Beckman Model K-75 Acralyzer was not delivered until after the conclusion of the field program. One-hour samples were collected in two midget impingers connected in series at flow rates of 200 ml per minute. The Saltzman solution in the impingers was modified by replacing the N(1-naphthyl) ethylenediamine hydrochloride (NEDA) normally used as the coupling compound with N (1-naphthyl, acetyl) ethylenediamine (ANEDA). The former reduces approximately 10% of the nitrogen dioxide to nitric oxide, thus giving low results for nitrogen dioxide and high results for nitric oxide. Less than 2% reduction takes place with ANEDA. The nitric oxide was oxidized to nitrogen dioxide with chromic oxide impregnated glass fiber filters placed between the two midget impingers. The absorbances of the resulting solutions were measured with a Bausch and Lomb Spectronic 20 using one-inch diameter tubes for improved sensitivity.

2.2.4 Total Hydrocarbons

Total hydrocarbons were monitored with a Beckman Model 108A Total Hydrocarbon Analyzer. The analyzer was calibrated daily using a Scott

"Close Tolerance" Analyzed Mixture of methane in hydrocarbon-free air for the span gas and Scott hydrocarbon-free air as the zero gas.

2.2.5 Individual C_1 to C_{10} Hydrocarbons

Samples were analyzed periodically for individual C_1 to C_{10} hydrocarbons using a Perkin-Elmer Model 900 Gas Chromatograph with dual flame ionization detectors and a sub-ambient temperature accessory. The C_1 to C_4 hydrocarbons were separated with a 1/8-inch column consisting of 21 inches of Porapak Q followed by 8 inches of silica gel. The C_5 to C_{10} hydrocarbons were separated with a 0.01 inch x 150 foot capillary column coated with Versilube F-50. Twenty five milliliter samples of air were concentrated directly on each column at -75°C. Liquid nitrogen, supplied through the sub-ambient accessory, was used to cool the column oven.

The following analytical cycle was employed:

1. Cool oven to -75°C and hold for several minutes with packed column valve in backflush position.
2. Inject sample into capillary column. (0 time)
3. Switch backflush valve to forward position at 170 seconds.
4. Inject sample into packed column at 180 seconds.
5. Raise temperature to -20°C at 240 seconds and hold for 60 seconds.
6. Program temperature from -20°C to 120°C at 8°C per minute.
7. Switch packed column to backflush at 1500 seconds.
8. Hold at 120°C to a total of 2000 seconds from injection.
9. Set oven temperature control to -75°C, air cool with oven lid raised for several minutes, and then close for liquid nitrogen cooling to -75°C.

The outputs of the two flame ionization detectors were recorded on a Texas Instrument dual pen recorder. The areas of the peaks from the

capillary column were measured and recorded with an Infotronics Model CRS-100 Electronic Digital Integrator-Printer with a tape accessory. The retention times and peak areas were printed as well as punched on tape for later computer calculation. In excess of 100 peaks were obtained in the C_5 to C_{10} range with a maximum sensitivity of less than 0.1 ppb. Excellent resolution was obtained so that concentrations of compounds eluting as little as three seconds apart could be determined. With this procedure it was possible for the first time to determine the entire range of hydrocarbons present in atmospheric samples and to accomplish this without external sample concentration.

The chromatographs were calibrated daily using multicomponent Scott Analyzed Gas Mixtures containing hydrocarbons which spanned the carbon number range eluted by each column.

2.2.6 Peroxyacetyl Nitrate

Peroxyacetyl nitrate was analyzed with an Aerograph Hy-Fi III Model 1220-1 Gas Chromatograph with an electron capture detector. A 1/8-inch x 1 meter column packed with 20% Carbowax 20M on Diaport S was operated at 40° C. The calibration standard was supplied by Dr. E. R. Stephens of University of California, Riverside.

2.2.7 Aldehydes

Formaldehyde, acrolein and total aliphatic aldehydes were determined periodically by standard wet chemical procedures[2]. The three samples were collected in midget bubblers simultaneously for one hour periods using a multi-stream sampler with separate orifices to control the flow rate to each set of bubblers. Formaldehyde was determined using the chromotropic acid method, acrolein was analyzed using the 4-hexylresorcinol method and total

aliphatic aldehydes were determined using the 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) method. The absorbances of the resulting solutions were measured with a Bausch and Lomb Spectronic 20 using one-inch diameter tubes for increased sensitivity. Calibrations were obtained from solutions containing known concentrations of formaldehyde and acrolein.

2.3 METEOROLOGICAL INSTRUMENTATION AT GROUND LEVEL

2.3.1 Temperature and Relative Humidity

Temperature and relative humidity were recorded by means of a Bendix Hygro-thermograph. The temperature sensor element of this instrument is a highly polished gold Bourdon tube. The humidity element is a multiple strand of specially treated hygroscopic human hair. Through a system of linkages these elements operate individual recorder pens.

The hygro-thermograph was used as a substitute for the Climet Wet and Dry Bulb Set which could not be obtained in time for use on the program. However, the latter, which gives more accurate and reliable measurements for humidity, has been received and will be used on future atmospheric surveys.

2.3.2 Wind Speed and Direction

Wind speed and direction were measured with a Climet 540-Degree Wind Recording System. This system combined low threshold, high sensitivity and accurate performance with an "ambiguous point logic" recording technique that eliminated the hard-to-interpret "crossover" region of conventional 0-360 degree polar wind systems. The transmitters were mounted on a mast 10 meters above ground. The data were recorded on separate Beckman recorders located in the trailer.

2.3.3 Ultraviolet Radiation Intensity

Solar ultraviolet radiation intensity was measured by means of a standard Eppley filter-photocell type UV photometer. The photometer was mounted on the roof of the trailer and had an unobstructed 180° view of the sky. The instrument was calibrated by the manufacturer before and after the test program. During the program the calibration was maintained by frequent checks against a standard tungsten-iodine lamp that was part of an Eppley test set. Because of a partial delivery by the manufacturer only one instrument was available for ground level use. It was moved from one site to the other during the sampling period.

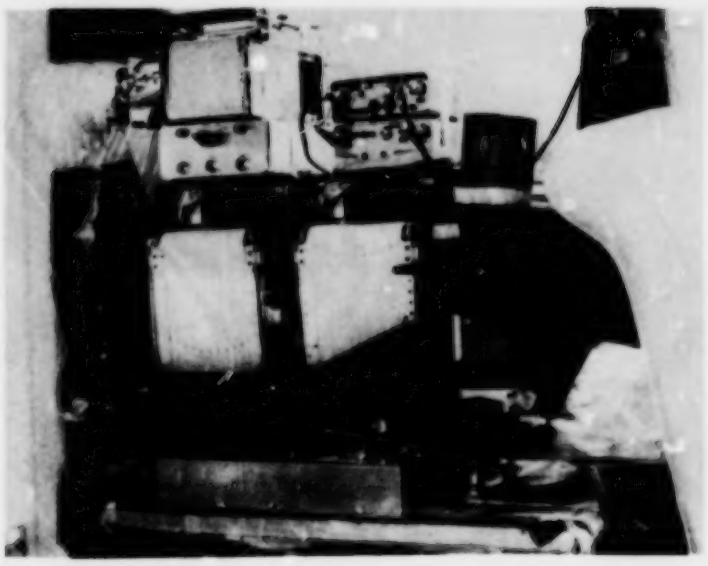
2.4 AIRCRAFT

A Waco Model 220-S aircraft was used as the platform for airborne measurements. This single engine, low wing, four-place light plane has the advantages of a large cabin, good low speed characteristics as well as a 160-mph cruise speed, and a 24-volt, 50-ampere electrical system. Convenient under-wing inspection plates were used to mount meteorological and UV sensors. Air sampling probes were mounted on the cabin roof and sample lines run from these probes into the cabin through existing ventilation ducts. The aircraft and some of the added instrumentation are shown in Figure 2-4.

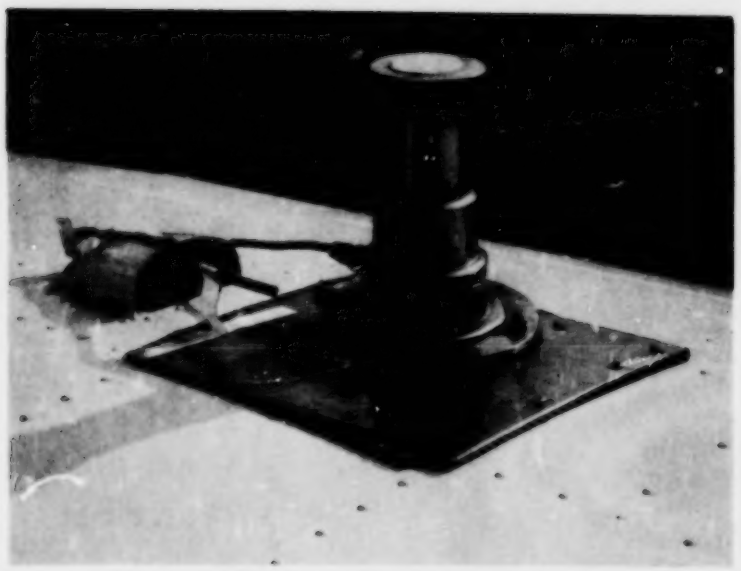
The aircraft was leased from Waco-Pacific Inc. and operated from their main hangar facility at Whiteman Air Park, Pacoima, California. The airport is located within convenient distance of Bolt Beranek and Newman's Van Nuys office. The aircraft was hangared to insure aircraft and instrument security.

Figure 2-4 Aircraft and Instrumentation

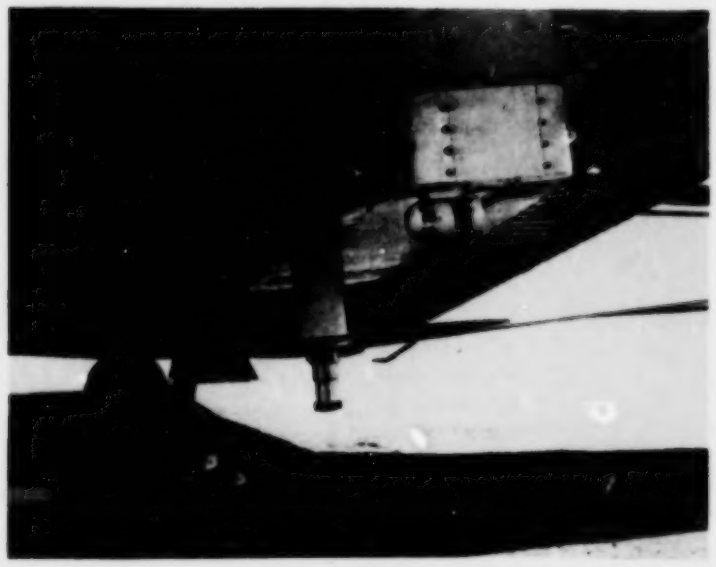
Waco Aircraft. Temperature Sensor Under Right Wing beside Pitot Tube



Recorders, Amplifiers and Controls Mounted Back of Pilot's Seat



UV Photometer (incoming UV) and Intake Tube for Bubblers, Oxidant and Bag Sampling Mounted on Top of Cabin



UV Photometer (outgoing UV) and Wet Bulb Temperature Sensor Mounted Under Left Wing

2.5 AIRBORNE INSTRUMENTATION

The instrumentation contained in the aircraft is summarized in Table 2-2.

The Waco has four wing inspection panels, two under each wing. Three of these panels were utilized for mounting sensors. Air temperature, relative humidity and outgoing UV sensors were mounted under the wings while the incoming UV sensor and two air sampling probes were mounted on the cabin roof. The Rosemount temperature probe was installed on the outboard panel under the right wing. The wet bulb thermometer was mounted on the outboard panel under the left wing. The outgoing UV sensor was mounted on the inboard panel under the left wing, oriented to look straight down and extended sufficiently below the wing surface such that when the landing gear was retracted, nothing interfered with its hemispherical view. The incoming UV sensor was mounted on a double plate, fastened above the cabin roof. It was oriented so as to look straight up when the aircraft was in level flight.

Aircraft power was utilized to operate the Mast oxidant detector and nitrogen oxide bubblers. The remaining instruments were powered by self-contained batteries. The right front seat was removed to make room for the UV recorders and Mast oxidant detector. Nitrogen oxide sampler and Tedlar bag storage was located behind the rear seat in the luggage area. Temperature, humidity and oxidant recorders and all instrument controls were mounted on the left rear seat. The observer sat in the right rear seat with easy access to all instrument controls and with all recorder traces in full view.

Table 2-2 Aircraft Instrumentation

Instrument	Parameter Measured
Rosemount - Platinum Resistance Thermometer	Air Temperature
Thermistor Wet Bulb Thermometer	Relative Humidity, Dew Point
Mast Microcoulumb Detector	Total Oxidant
Eppley Ultraviolet Photometers	Incoming and Outgoing Ultraviolet Radiation - 300-400 nm Spectral Response
Nitrogen Oxides Bubblers	NO and NO_2
Six-Liter Tedlar Bags	Individual Hydrocarbons, Carbon Monoxide
Aircraft Instruments	Aircraft Parameters - Airspeed, Altitude, Heading, Attitude, Time

2.6 AIRCRAFT SAMPLING AND MEASUREMENT TECHNIQUES

One of the air sampling probes mounted on the cabin roof was directed forward such that ram pressure pushed sample air through it. Air from this probe was directed through Teflon tubing to an expansion chamber where it was decelerated to cabin pressure. A small Teflon tube placed at 90^{o} to this low velocity stream carried an air sample to the Mast oxidant meter. The Mast air inlet was immersed in sample air at cabin pressure, which gave an abundance of sample air with no pressure fluctuations across the oxidant detector. The Tedlar bags were filled with air samples from this same ram pressure line by temporarily disconnecting the tube from the expansion chamber and directing it into a bag. The samples collected in Tedlar bags were protected from UV radiation by placing them in a large opaque black plastic pouch. The bag samples were analyzed on the ground for carbon monoxide and individual C_1 to C_{10} hydrocarbons.

A second air inlet mounted above the cabin air scoop was connected to the nitrogen oxide bubblers by Teflon tubing. This air inlet was carefully "tuned" so that no pressure differential existed between the cabin and the air inlet. The vacuum pump on the NO_x bubbler exhaust side then provided the only means for moving air through the samplers. Air was passed through the bubblers for at least 15 minutes to insure an adequate sample. The nitrogen oxides samples were collected at the same altitudes as the Tedlar bag samples.

Air temperature, dry and wet bulb, incoming and outgoing ultraviolet radiation flux were measured continuously and recorded on strip charts. The altitudes were hack marked on the temperature recorder and the time recorded on the observer's flight log. The voice recorder was used to

record observations and other pertinent remarks. Visual observations of smog conditions were supplemented with approximately 180 35mm color photographs.

2.7 DATA REDUCTION

The continuous monitoring data were recorded on strip charts. Half-hourly averages were determined by a manual procedure, and the analog data were converted into digital form on paper tape for further processing and print out.

Approximately 109 peaks for C_5 to C_{10} hydrocarbons were obtained from the capillary column of the Perkin-Elmer chromatograph. The retention time and area of each peak were measured and the data were punched on paper tape using the Infotronics Integrator-Printer with tape accessory. A logical procedure was devised for computer identification of each of 109 peaks in a chromatogram. The punched tape output of the chromatographic system was processed to print out the concentration corresponding to each peak as it was identified by comparison of the sample retention time with a file of standard retention times. Provisions were included to accomodate variations in peak retention time.

The peak areas for the C_1 to C_4 hydrocarbons were obtained by manual measurement of the chromatographic peaks. Concentrations were determined with a desk calculator. The remainder of the periodic data, which included that from the colorimetric analyses and the CO and PAN chromatographs, were also calculated manually.

The strip charts obtained during aircraft flights were processed as follows. Recorded temperature traces were scaled, converted to physical

units, and corrected for the slight warming of ram-air at aircraft speeds. Wet bulb temperatures were converted to dew point using the standard psychrometric equation which required the appropriate dry bulb reading and the ambient pressure-altitude.

Incoming ultraviolet readings were examined for aircraft wing-wavering since the total incoming flux is sensitive to the horizontal orientation of the observing platform. Aircraft observer notes, corresponding to selected altitudes when level flight was maintained for this purpose, were used to determine the proper UV value from the recorder trace. Outgoing ultraviolet values were much less sensitive to plane orientation and therefore, easily reduced from the chart.

3. PROGRAM DESIGN AND OPERATIONS

The field operations program was designed to obtain comprehensive aerometric data at two ground level sites during the period from August 22 to November 15, 1968. Airborne measurements to establish vertical gradients above the ground sites were to be obtained on approximately fifteen selected days. The data were to include primary pollutants, photochemical products and meteorological factors which affect the rates of photochemical reactions and transport of pollutants.

3.1 TEST SITES

The criteria for selection of ground level sites were that the sites be along reasonable air trajectories into the Azusa area, and that one site be at or near an airport to facilitate transfer of airborne samples. It was also desirable that one site be in an area where morning pollutant concentrations were high and the other site be in an area where high oxidants were frequently recorded.

These criteria were met by setting up the customer trailer in a building on Salt Lake Avenue in Huntington Park and the Scott trailer at the El Monte airport. These two sites were situated 12.7 miles apart, and the Huntington Park site was located such that a 230° wind would carry its air parcel to the El Monte site. This corresponded well to the prevailing late morning and afternoon wind direction on high oxidant days which averaged 240° at each site.

3.2 TEST PROGRAM AT GROUND SITES

It was desirable to follow the composition of an air mass from the

time its pollutant components were emitted until the photochemical products formed passed their peak. Therefore, periodic sampling and analysis at Huntington Park was carried out from 0500 to 1400 PST, and at El Monte it was conducted from 0700 to 1600 PST. This enabled us to follow the pollutant buildup at Huntington Park which reached its peak between 0600 and 0800 PST and to thoroughly cover the oxidant maximum which was usually recorded between 1130 and 1300 PST at Huntington Park and between 1300 and 1430 PST at El Monte.

The periodic samples were collected and analyzed at approximately one hour intervals. This represented the time needed to obtain sufficient sample for the wet chemical analyses and to recycle the chromatograph for the individual hydrocarbon analyses. Airborne samples were analyzed for hydrocarbons at the site over which they had been collected. All airborne samples for carbon monoxide and nitrogen oxides were analyzed at El Monte. Calibrations and blanks were run frequently to insure valid data.

3.3 AIRBORNE PROGRAM

On days when moderate to heavy smog was forecast, aircraft flights were scheduled for morning and afternoon. The scheduling was such as to catch the early to mid-morning hydrocarbon peak and early afternoon oxidant peak. The flight plan, which is illustrated on the map in Figure 3-1, consisted of take-off from Whiteman Air Park, thence via the high pass at Tujunga-LaCanada or through the San Fernando Valley over Burbank to Stadium Intersection (Los Angeles Coliseum) arriving over Stadium at 5000 ft. A descent was made to 1500 ft (min. allowable altitude) and samples were taken on a race track turn flying as close to Huntington Park as possible and back

Figure 3-1 Aircraft Flight Plan

to Stadium Intersection. A Tedlar bag was filled and the nitrogen oxide bubblers were run for 15 minutes at 1500 ft. If below the inversion top, a climb to 2/3 distance from ground to inversion top was made and Tedlar bag and NO_x samples taken. While climbing and descending the aircraft leveled off at 1000 ft. intervals to align the UV sensors vertically and long enough to stabilize the UV recorder trace. The time and altitude hack were also put on the charts. The aircraft climbed until it was clearly above the inversion top and then headed for El Monte where it descended to a touch-and-go landing at El Monte airport. It then proceded to the gravel pit area 2 miles east of the airport and collected Tedlar bag and NO_x samples at 1/3 and 2/3 distance between ground and inversion top. The aircraft returned to land at El Monte and dropped the Tedlar bag samples and NO_x bubblers for analysis. The crew then picked up supplies and material for the next flight.

Deviations from the standard plan were made when special conditions warranted. Smog fronts were considered of special importance and were penetrated and investigated on three occasions. The smog front locations were carefully located by ground reference entries in the flight log. Horizontal penetrations were made through the leading edges of the front while recording continuous data. Tedlar bag and NO_x samples were collected on both sides of the front.

4. DESCRIPTION OF DATA FILE

The data obtained in this program can be placed in four categories: continuously recorded chemical and meteorological elements obtained at the two ground stations, chemical and meteorological data obtained from the airborne platform, periodic data sampled during selected intervals at the ground stations, and gas chromatographic hydrocarbon data.

A summary of the quantity of data recorded continuously at the two ground stations is presented in Table 4-1. Half-hourly averages were centered about the hour and half-hour. Although the instruments were in continuous operation, measurements of ozone as distinct from total oxidant were made only at selected intervals; measurements of ultraviolet flux were made by one instrument mounted on top of the mobile station at El Monte for most of the data gathering period. It was moved to Huntington Park station during the latter part of the period. The number of points presented in this category total 29,000.

The scope of the flight program is summarized by a compilation of facts and figures in Table 4-2, Summary of Flight Program. Of the 37,500 values recorded by the flight instruments, 12,000 values were judiciously selected for processing and presentation. Carbon monoxide and nitrogen oxide values for the airborne samples analyzed on the ground were interposed in their proper chronological sequence in the flight data. Aircraft observer notes and comments were edited and placed in their proper position during the final collation of the data files.

Periodic analyses for aliphatic aldehydes, formaldehyde, acrolein, nitric oxide, nitrogen dioxide and total nitrogen oxides were made at Huntington Park from August 22 to November 13 and at El Monte from

Table 4-1 Continuously Recorded Elements at Ground Stations

Element	Period Covered Month/Day	No. Days	No. Averages Per Hour	No. Tabulated Points
Huntington Park				
Wind speed	9/4 - 11/12	69	2	3,300
Wind direction	9/4 - 11/12	69	2	3,300
Temperature	9/27 - 11/12	46	1	1,100
Relative humidity	9/27 - 11/12	46	1	1,100
Ultraviolet flux	11/5 - 11/12	7	2	100
Total oxidants	9/4 - 11/12	69	2	3,300
Ozone	10/9 - 11/12	20	2	270
Total hydrocarbons	9/23 - 11/12	50	2	2,400
Carbon monoxide	9/9 - 11/12	64	2	3,070
Total Huntington Park:		440		18,040
El Monte				
Wind speed	9/21 - 11/15	56	2	2,700
Wind direction	9/21 - 11/15	56	2	2,700
Temperature	9/28 - 11/15	48	1	1,150
Relative humidity	9/28 - 11/15	48	1	1,150
Ultraviolet flux	10/1 - 11/5	36	2	500
Total oxidants	9/23 - 11/15	53	2	2,500
Ozone	10/10 - 11/15	30	2	350
Total El Monte:		327		11,050

Table 4-2 Summary of Flight Program

Principal flight routes: Whiteman Air Park, Huntington Park, El Monte.

Period covered: August 31 to November 11, 1968

Number of days when flights occurred: 18

Total number of flights: 24

Approximate hours aloft: 55

Continuously recorded elements: temperature, wet bulb, oxidants, incoming ultraviolet and outgoing ultraviolet.

Number of Tedlar bag samples for carbon monoxide and hydrocarbons: 70

Number of bubbler samples for nitrogen oxides: 35

Total number of values processed from charts: approximately 37,500

Total number of values reduced from charts: approximately 12,000

Total number of data points reduced: approximately 7,100

September 23 to November 14. Periodic carbon monoxide measurements were made at El Monte from October 1 to November 8. A total of approximately 2,600 values were generated from the periodic analyses.

A total of 270 chromatographic analyses for individual C_1 to C_{10} hydrocarbons were carried out. Of these approximately 100 were performed at each site on ground level samples and the remaining 70 represented airborne samples. The identification of 100 peaks per chromatogram along with an equal number of concentration determinations resulted in 54,000 point values.

The total number of data points obtained in the program is summarized below.

PROGRAM TOTAL DATA POINTS

	Measured	Presented
Aircraft data (1)	37,500	12,000
Ground data (2)	37,000	29,100
Periodic data (3)	2,600	2,600
Chromatogram data (4)	54,000	54,000
	131,100	97,700

(1) based on 100-ft. altitude increments

(2) based on half-hourly averages

(3) measurements at selected times

(4) aircraft bag samples and ground samples at selected times

5. DISCUSSION OF DATA COLLECTED

The massive volume of data collected during the period from August to November 1968 illustrates the extreme complexity of the Los Angeles Basin atmosphere. While certain diurnal trends and a few direct relationships are apparent, it is obvious that any reasonably concise definition of the photochemical system will require not only the in-depth analysis of the 1968 data which is currently in progress as Phase II, but detailed analyses of even more comprehensive select data collected in future surveys.

The basin atmosphere may be described as a vast non-homogeneous air mass whose composition is controlled by a large number of variables which affect the rate at which contaminants are added, the rate at which contaminants and photochemical products are removed, and the rate at which chemical and photochemical reactions proceed. The rate at which contaminants are emitted into the atmosphere is subject to substantial diurnal variation because motor vehicles, which are a primary source of emissions, are operated in much greater numbers during early morning and late afternoon rush hours. Atmospheric ventilation is controlled by meteorological factors such as wind speed, turbulence, inversion height and temperature. Reactions rates are affected primarily by the composition and concentration of hydrocarbons and nitrogen oxides present, the ultraviolet radiation intensity, temperature and humidity.

Factors which affect the transport of pollutants within the basin air mass are also important because the manifestations of smog observed at a particular point are frequently caused by contaminants which emanated ten to twenty or more miles away. Since many reactions which lead to

photochemical products proceed slowly, the concentrations present at a particular time and place are a function of all factors to which the particular parcel of air has been exposed from the time its contaminants were emitted rather than of the conditions existing at the instant in question. This points out the need to study atmospheric data on a real time basis. Data averaged over a number of days or an entire season show trends and relationships which may be coincidental and they tend to hide the true relationships between variables.

In order to illustrate atmospheric behavior on high oxidant days the complete ground level data for October 22 and 23, two days in the middle of a major smog episode, are given in Tables 5-1 and 5-2. The data for oxidant, nitrogen oxides, carbon monoxide and wind speed for October 18, 22, 23, 24 and 28 at both ground sites are plotted in Figures 5-4 through 5-13 to further depict the variations in diurnal patterns which occur from day to day. The individual data elements will be discussed separately. While the comments will apply to the entire sampling period, emphasis will be placed on the specific days illustrated.

5.1 OXIDANTS AND OZONE

The maximum half-hourly oxidant averages at each site for each day in the period from September 23 to November 13 are plotted in Figure 5-1. It can be seen that the major smog episodes in order of decreasing severity were October 21 to 28, September 24 to 27, November 9 to 10 and October 5. The maximum half-hourly values were equal to or greater than 15 pphm at both sites on each of these 15 days. The oxidant values were usually higher at El Monte than at Huntington Park, but the day to day trends for the two sites were similar.

Ozone concentrations at Huntington Park, as measured by olefin titration, were 2 to 4 pphm less than oxidant readings when the oxidant was less than 15 pphm, and they were from 5 to 8 pphm less when the oxidant ranged from 15 to 26 pphm. A smaller difference was recorded at El Monte where ozone was 1 to 2 pphm less than oxidant when the oxidant was less than 15 pphm and 3 to 5 pphm less when oxidant read from 15 to 35 pphm. It is assumed that the differences represent nitrogen dioxide, peroxyacetyl nitrate and other oxidizing materials to which the Mast instrument responds. Tests showed that the response to nitrogen dioxide was 8% that of ozone. Response factors for other compounds were not determined.

The time of day at which peak oxidant was recorded is shown in Figure 5-2. The oxidant maxima at Huntington Park occurred most frequently at 1200 PST. A secondary peak in the frequency chart is present at 1430 PST. The distribution around 1200 PST represents days on which the prevailing late morning wind carried the pollutants away in the direction of El Monte while the maxima around 1430 PST are typical of low oxidant days where the level increased gradually throughout the day. The oxidant exceeded 11 pphm on only one day with a late afternoon maximum. The oxidant maxima at El Monte occurred most often at 1330 PST. This represented the time at which the pollutants transported from the Huntington Park area reached their greatest concentration. It is interesting to note that at 1330 PST the frequency curve for Huntington Park reached a minimum value.

On most days the oxidant maxima at Huntington Park were reached after the hydrocarbon and nitrogen oxide concentrations began to decrease through atmospheric dilution. High oxidant levels frequently persisted for 2 to 3 hours at contaminant concentrations which were less than 20% of

the 0600 to 0800 values as illustrated in Figures 5-7, 5-9 and 5-11.

At El Monte oxidant readings usually began to increase between 0900 and 1000 as the consequence of local early morning pollution. Oxidant increased rapidly upon arrival of the pollution from the Huntington Park area. The oxidant peak coincided with the secondary contaminant peak contributed by the incoming air parcel. However, contaminant concentrations at the time of oxidant maxima usually were lower than during the early morning peak period as shown in Figures 5-6, 5-8, 5-10 and 5-12. The reason for the typical sharp decrease in oxidant at El Monte from 1500 to 1700 PST will require further analysis of the data.

5.2 CARBON MONOXIDE

In studying a photochemical system carbon monoxide measurements are primarily useful as a tracer of automotive exhaust emissions. Carbon monoxide is photochemically inert and essentially all of it found in urban atmospheres is contributed by vehicular exhaust. Readings in the Los Angeles Basin serve to indicate the rate of horizontal transport and vertical diffusion of exhaust contaminants. Ratios of hydrocarbons and nitrogen oxides to carbon monoxide assist in evaluating the relative contribution of evaporative fuel and solvent hydrocarbon sources and stationary sources of nitrogen oxides.

Maximum carbon monoxide concentrations were normally found between 0630 and 0730 PST at both El Monte and Huntington Park. The greater vehicle density in the Huntington Park area resulted in peak concentrations two to three times those found at El Monte. By 0900 PST the concentrations at both sites had usually decreased to less than half the peak values.

High late-night (2200 - 0130 PST) concentrations were noted occasionally at Huntington Park. The frequency of high night-time carbon monoxide increased toward the end of the test period to the extent that it was a common occurrence in November.

A sharp early afternoon rise in carbon monoxide at El Monte after a drop from the early morning peak heralded the arrival of polluted air from the southwest. This is shown in Figures 5-6, 5-8, 5-10 and 5-12.

5.3 NITROGEN OXIDES

Nitric oxide and nitrogen dioxide play prominent roles in photochemical smog formation. The photolysis of nitrogen dioxide by ultraviolet radiation produces oxygen atoms which initiate a series of reactions which lead to the various products associated with photochemical smog. Nitric oxide is converted to nitrogen dioxide in the process, and this conversion must be nearly complete before noxious products such as ozone and peroxyacyl nitrates are formed. Thus, nitric oxide inhibits the reactions which produce smog, and any decrease in its rate of conversion to nitrogen dioxide will reduce or at least delay the appearance of most smog manifestations. Nitrogen oxides also take a direct part in the secondary reactions which produce organic nitrates and peroxy nitrates.

Maximum nitrogen oxide concentrations were found during the same early morning period as peak carbon monoxide concentrations indicating that vehicular exhaust is a major contributor at that time. However the peak for nitrogen oxide usually occurred from 1/2 to 1 hour later than the carbon monoxide peak. The ratio of nitrogen oxides to carbon monoxide varied to some extent from day to day as seen in Figures 5-4 through 5-12.

The ratio was usually higher at El Monte than at Huntington Park. The differences in ratios could be caused by greater relative contributions of nitrogen oxides by stationary sources at El Monte or differences in area driving habits. Day to day variations in ratios could be caused by the effect of meteorological factors, such as wind direction and diffusion rate, on the dispersion of stationary source emissions. Surprisingly, no changes in nitrogen oxide to carbon monoxide ratios during individual days were noted, although the ratio was usually slightly higher during the morning traffic peak than later in the day. This suggests that most of the nitrogen oxides consumed in atmospheric reactions were replaced by fresh emissions from stationary sources. This demonstrates a distinct difference between the atmosphere and laboratory systems where substantial amounts of nitrogen oxides are consumed as the experiments proceed.

Nitric oxide accounted for approximately 80% of the total nitrogen oxides in samples collected before 0700 PST. This was expected because nitric oxide predominates in the major emission sources. After 0700 the nitric oxide was converted to nitrogen dioxide as the solar UV intensity increased and photochemical reactions occurred. One objective of this program was to determine the rate of this conversion in the atmosphere. A typical rate on high oxidant days was 1 ppb per min. during the interval until 75% had been converted. The remainder of the nitric oxide was converted more slowly, and from 5 to 10% remained as nitric oxide even during high oxidant periods. On low oxidant days, when low UV intensity or rapid dispersion were common, the rate was often less than 0.5 ppb per min. On a few occasions the rate appears to have exceeded 1.5 ppb per min. A more detailed analysis of the present data and the

availability of a continuous monitoring instrument in future work should yield more precise rate data.

For the present we can express the nitric oxide conversion rate in a more meaningful manner in terms of the time to an increase in oxidant which signifies nearly complete conversion. On most days this increase in oxidant occurred between 0900 and 0930 PST at both sites. This means that 2 to 2 1/2 hours were required from the 0700 pollutant peak. The average UV radiation intensity during this period was less than half of the mid-day value. This strongly suggests that radical changes would have to be made in emissions if a condition of incomplete nitric oxide conversion in the Los Angeles Basin atmosphere is to be reached.

5.4 TOTAL HYDROCARBONS

Total hydrocarbon concentrations are often used as a measure of pollution level even though a large portion of the response is usually due to hydrocarbons which do not take part in photochemical reactions at significant rates. The data obtained at Huntington Park incorrectly indicated that total hydrocarbons remained relatively constant on many days when the total concentration of individual hydrocarbons determined by chromatography changed drastically. This was caused by electronic damping of the instrument signal when the signal was greater than half scale (0.5 volt = 10 ppm carbon). Therefore all data collected above 8 ppm carbon should be disregarded. The instrument will receive a thorough check out before the start of any future program.

5.5 INDIVIDUAL C_1 TO C_{10} HYDROCARBONS

The availability, for the first time, of data for the complete

range of hydrocarbons in a polluted atmosphere offers a means of gaining much additional insight into the sources of pollutants, relative source strengths, and the extent to which photochemical reactions have proceeded. Much of this knowledge will be obtained in the detailed data analysis which is now in progress. Present comments will be limited to those facts which may be noted by a thorough eyeballing of the data.

A complete tabulation of the data from four chromatograms obtained on October 22 is given in Table 5-3. As would be expected, the hydrocarbon composition of the atmosphere during the early morning contaminant peak strongly resembled that of auto exhaust. In addition, the high concentrations of light paraffins, which have been reported by previous investigators, are quite evident. The concentrations of these paraffins, which include methane, ethane and propane, change independent of the concentration changes in the auto exhaust components from day to day and within individual days. Additional data analysis relating light paraffin concentrations to atmospheric transport and dispersion factors should indicate whether their source is widespread, e.g. natural gas leaks, or localized, e.g. oil field losses.

During the period following 0700 PST, photochemical reactions, triggered by the UV radiation induced photolysis of nitrogen dioxide, consumed hydrocarbons at varying rates depending on their reactivity. The internal olefins, such as 2-methyl-2-butene, had essentially disappeared, and concentrations of terminal olefins had been substantially reduced by the time oxidant began to increase. This indicates that the less reactive hydrocarbons, which are present in relatively high concentrations, play an important role in reactions which occur during the

period that peak oxidant is recorded. It can be seen that the di- and tri-substituted aromatics also disappear at significant rates. The disappearance of saturates and mono-substituted aromatics is too slow to be determined by visual inspection of the data.

The extent to which photochemical activity has proceeded may be determined from the ratios between moderately reactive and unreactive or slightly reactive hydrocarbons emanating from the same source. The ratios of 1-hexene to hexane, mesitylene (1,3,5-trimethylbenzene) to n-propylbenzene and m + p-xylene to ethylbenzene merit further study. A knowledge of the average irradiation time for a typical polluted air parcel at peak oxidant will permit the establishment of a realistic reactivity scale. It will differ from scales currently in use which are based on initial reaction rates and thereby show unrealistically high relative contributions by the very reactive hydrocarbons.

The hydrocarbon - nitrogen oxide ratio is known to affect reaction rates in laboratory photochemical systems. The ratio of reactive hydrocarbons to nitrogen oxides during the morning peak period was approximately 3 to 1. In addition to reducing emissions, it is desirable that control methods change this ratio in the direction of slower reaction rates. A detailed analysis of the effect of the varying day to day ratios noted at Huntington Park should define ratio effects and assist in evaluating suggested control measures such as nitrogen oxide reduction.

The ratios between unreactive or slightly reactive hydrocarbons which are characteristic of different sources can be used to estimate relative source strengths. Excellent correlation was found between carbon monoxide and acetylene indicating that either may be used as an indicator

of auto exhaust concentration. Since n-butane is a prominent component of automotive evaporative emissions which involve fractionation of the fuel, the increase in the n-butane to acetylene ratio which occurs from morning to afternoon samples would be expected to represent a measure of automotive evaporative losses. Additional information can be obtained from a study of ratios between hydrocarbons representative of different classes and carbon number ranges. Evaporative emissions involving the entire fuel are nearly impossible to distinguish from exhaust emissions without additional data on individual hydrocarbon to acetylene or carbon monoxide ratios measured on a sample of vehicles in on-the-road operation.

5.6 PEROXYACETYL NITRATE

Peroxyacetyl nitrate and its homologs are known to cause eye irritation and plant damage. The concentrations present in photochemical smog are of considerable interest. Unfortunately, the delay in obtaining a calibration standard for this unstable material and problems with losses in the chromatograph injection block led to highly erratic data for this compound. It was found that the original identification of a particular chromatographic peak as PAN was erroneous. Therefore, no data for PAN are included in our final report. The problems have been corrected and no difficulty is anticipated in collecting PAN data in future programs.

5.7 ALDEHYDES

Formaldehyde and acrolein are components of automotive exhaust as well as photochemical products. Both are known to be eye irritants. The maximum concentrations found during smog episodes were approximately

10 pphm formaldehyde and 1 pphm acrolein. There is some question as to whether these concentrations would be sufficient to be major contributors to the eye irritation experienced during these periods.

The maximum concentrations at Huntington Park were recorded in the late morning prior to the oxidant maxima. It seems reasonable that concentrations of these products decreased before the oxidant maxima. The rate of formation of ozone, an indirect product of hydrocarbon reactions, would be affected less by dilution of hydrocarbons than that of aldehydes which are direct products. It is estimated that at least 80% of the aldehydes present at peak concentrations was contributed by photochemical reactions. Maximum aldehyde concentrations at El Monte were slightly less than those at Huntington Park. The aldehyde maxima at El Monte were recorded at the same time as the oxidant maxima since they were both greatly enhanced by the influx of polluted air from the Huntington Park area.

5.8 TEMPERATURE AND RELATIVE HUMIDITY

The effect of temperature and relative humidity on photochemical processes in the Los Angeles Basin is not known. It is known that higher temperatures speed up some of the reactions, and that high oxidant is usually recorded on hot days. The comparison of maximum temperature with maximum oxidant for individual days in the test period, shown in Figure 5-3, tends to discount a direct relationship between temperature and oxidant. It is more likely that meteorological conditions which promote smog episodes also favor high temperatures. Recent laboratory studies have indicated that relative humidity can have a pronounced effect on photochemical reactions.

However the role of humidity in atmospheric reactions has not been established.

5.9 WIND SPEED AND DIRECTION

Wind speed and direction control the transport of pollutants which has been referred to frequently in previous sections. In addition, wind speed plays a major role in the rate of diffusion of pollutants into the upper atmosphere. The duration of the period of light (<2 mph), variable wind after the morning contaminant peak at Huntington Park greatly influenced the maximum oxidant produced. Figures 5-4 through 5-13 show that the contaminant concentrations at Huntington Park decreased sharply with increasing wind velocity, and the concentrations at El Monte increased sharply soon after the wind velocity increased. Low oxidant was recorded on days when the wind speed reached 3 mph or greater within one hour after the morning contaminant peak.

5.10 ULTRAVIOLET RADIATION

Ultraviolet radiation initiates the whole series of reactions which produce photochemical smog. This is accomplished primarily through the photolysis of nitrogen dioxide although other atmospheric pollutants are known to absorb UV radiation to a lesser degree. The diurnal pattern of UV radiation intensity changed very little. No changes in photochemical reaction rates or product concentrations due to variation in UV intensity were noticeable upon visual inspection of the data.

5.11 AIRBORNE DATA

A total of 24 flights were flown on 18 days. An extensive

analysis of the approximately 12,000 data points which have been reduced must be completed before a detailed discussion of the airborne work can be presented.

This includes the definition of the nature and location of the inversion layer which varied from flight to flight as shown by the vertical profiles obtained at Whiteman and El Monte. The interpretation of the airborne data will be an important segment of the Phase II work.

The level of contaminants present during morning flights was generally very low with the carbon monoxide concentration rarely exceeding 1 ppm. Despite this fact, oxidant readings were often in 5 to 10 pphm range as compared to 1 to 2 pphm at ground level. This appears to confirm the validity of ground level observations that high oxidant can be present even though contaminant levels are relatively low. Highest oxidant concentrations were found at the inversion interface. At times flying restrictions over Huntington Park did not permit collection of data below the inversion.

Sometimes the inversion was sharply defined by the vertical temperature profiles, but on other occasions the layer was diffuse and ill-defined. The inversion appeared to be located at a constant height above mean sea level over the entire basin. This meant that the height of the layer above ground level was less at higher ground elevations.

The picture was usually different during the afternoon flights. The vertical profile over the El Monte area showed good homogeneity from ground level to 1500 or 2000 feet with later evidence of the presence of an inversion. Concentrations of oxidant and contaminants in the airborne and ground level samples were comparable. In some cases it was difficult

to distinguish between chromatograms of samples collected at ground level and at 1500 feet. This indicates that the morning pollution from the Huntington Park area was thoroughly mixed into the lower atmosphere while it was being transported to El Monte.

The hydrocarbon composition of airborne samples, collected both above and below the inversion, was radically different than that of ground samples on frequent occasions. The airborne samples contained relatively high concentrations of C_5 to C_8 branched-chain paraffins and C_7 and C_8 aromatics. The toluene to benzene ratios varied from 15-1 to 30-1 as compared to 2-1 for the ground sample. This composition best matches that of the fuel used by high performance piston engine aircraft. This is not too surprising since the Huntington Park area is in the landing pattern for Los Angeles International Airport. A similar composition was also found in some airborne samples collected over El Monte, but no evidence of contribution of this source to ground level pollution has been found in the chromatograms from either station.

It was observed that the smog took the form of clouds which contained visible voids in which low oxidant values were recorded. Oxidant was generally much higher at the leading edge of smog fronts than within the smog clouds. The visual observations made will be a valuable source of information in interpreting the airborne data.

The determination of wind direction and velocity at flight altitudes by means of "wind stars" proved to be meaningless because of the extremely light wind conditions encountered during the flights.

5.12 DISCUSSION OF DATA FOR SELECTED DAYS

The individual elements have been discussed for the selected days illustrated in Figures 5-4 through 5-13 and Tables 5-1 through 5-3 in previous sections. We will now look at these days from a broader viewpoint.

October 22 and 23 were both days of high contaminant and high oxidant concentrations. October 22 shows the simpler diurnal pattern. The morning contaminants remained in the Huntington Park area until approximately 1030 PST when the wind increased and a sharp reduction in contaminants occurred. By 1030 oxidant formation was well under way, and oxidant continued to increase after contaminant dilution had begun. The oxidant peak was reached at 1130 PST, and it persisted for several hours thereafter. At El Monte oxidant formation due to local pollution was also well under way by 1030. The arrival of the polluted air mass from the direction of Huntington Park greatly enhanced oxidant formation and a maximum of 35 pphm was reached at 1330.

On October 23 the wind at Huntington Park remained light and from the north to northeast for much of the morning. Initially this drove the contaminants to the southwest, and when the wind finally shifted to the prevailing southwesterly direction, it passed back over Huntington Park and caused a sharp rise in both contaminants and oxidant at 1230 PST. At El Monte the oxidant produced from local contaminants reached 12 pphm at 1030 and remained relatively constant until 1330. At this time the high pollution arrived from the southwest, and the oxidant increased to 30 pphm at 1430.

On October 24 the early morning concentration of contaminants at Huntington Park was higher than on the previous days probably reflecting

transport from the downtown area by the northerly wind. The mid-morning wind speed of 2 to 3 mph not only drove the pollution to the south but also dispersed it to a greater degree than the 1 mph wind of the previous day. When the wind eventually increased and shifted to the southwest, the air parcel had been diluted to the point that only a nominal increase in oxidant from 8 to 15 pphm occurred upon its arrival at El Monte. However, the oxidant persisted longer at El Monte than on the previous days probably because the contaminants had been dispersed throughout a larger air mass.

The patterns on October 18 and 28 were considerably different than those just discussed. On the 18th the contaminant levels at Huntington Park were high from 0800 to 0830 PST. They were then rapidly dispersed by a 4 mph wind from the north. The pollution level remained low for the remainder of the day, and the maximum oxidant was only 4 pphm. The possibility of inhibition by the high nitrogen oxide to hydrocarbon ratio is being studied. A somewhat similar pattern was followed at El Monte where the oxidant maximum was 13 pphm. It is difficult to explain why the oxidant decreased while the nitrogen oxides were increasing during the period from 1300 to 1400. Hydrocarbon and carbon monoxide data are not available for this interval.

The typical early morning carbon monoxide and hydrocarbon peaks did not occur at Huntington Park on October 28, and their concentrations remained relatively the same throughout the morning. The fact that this was the first working day after the return to standard time may have spread out the traffic load. A heavy fog which persisted past 1000 PST delayed the start of photochemical reactions. The oxidant rose sharply

after 1200 and reached a peak of 15 pphm at 1330. Its sharp decline between 1330 and 1400 cannot be explained at this time. The morning wind speed and direction at El Monte varied widely. This appeared to cause the contaminants to arrive in batches, but their concentrations remained sufficiently high to maintain the oxidant above 15 pphm for a 2 1/2 hour period.

The above discussion may not adequately define the aerometric events which took place on the five selected days. However, it should serve to demonstrate the complexity of the atmosphere and illustrate a few of the many diurnal patterns which occur during the smog season.

5.13 SUMMARY

The most important fact that is demonstrated by the aerometric data is the vast difference between the atmospheric system and laboratory systems. While the same reactions take place in both systems, there is a delicate balance between a large number of competing reactions. Laboratory experiments are valuable for identifying these reactions and measuring their kinetic rates under controlled conditions, but any attempt to predict the effects of reducing various inputs to the atmosphere based only on laboratory data is subject to gross error. Since most control efforts are quite costly, it is most desirable to obtain evidence that they will reduce noxious photochemical products in the atmosphere before putting them into effect. A study of the atmospheric system is limited by the inability to control the input to the system. However the data plotted in Figures 5-4 through 5-13 show that the concentrations of contaminants and the ratios between them varied considerably from day to day. The range

appears adequate to determine effects of changing specific input concentrations and ratios.

In addition to defining atmospheric reaction rates and developing relationships between various contaminants, Phase II of the program, the analysis of the 1968 data, will provide a firmer basis for evaluating most important factors to be measured, the critical periods during which measurements should be made and the location of the sampling points.

The final report on Phase II will be available in approximately two months.

Figure 5-1 Maximum Half-hourly Oxidant Values For Period 9/23/68 to 11/13/68

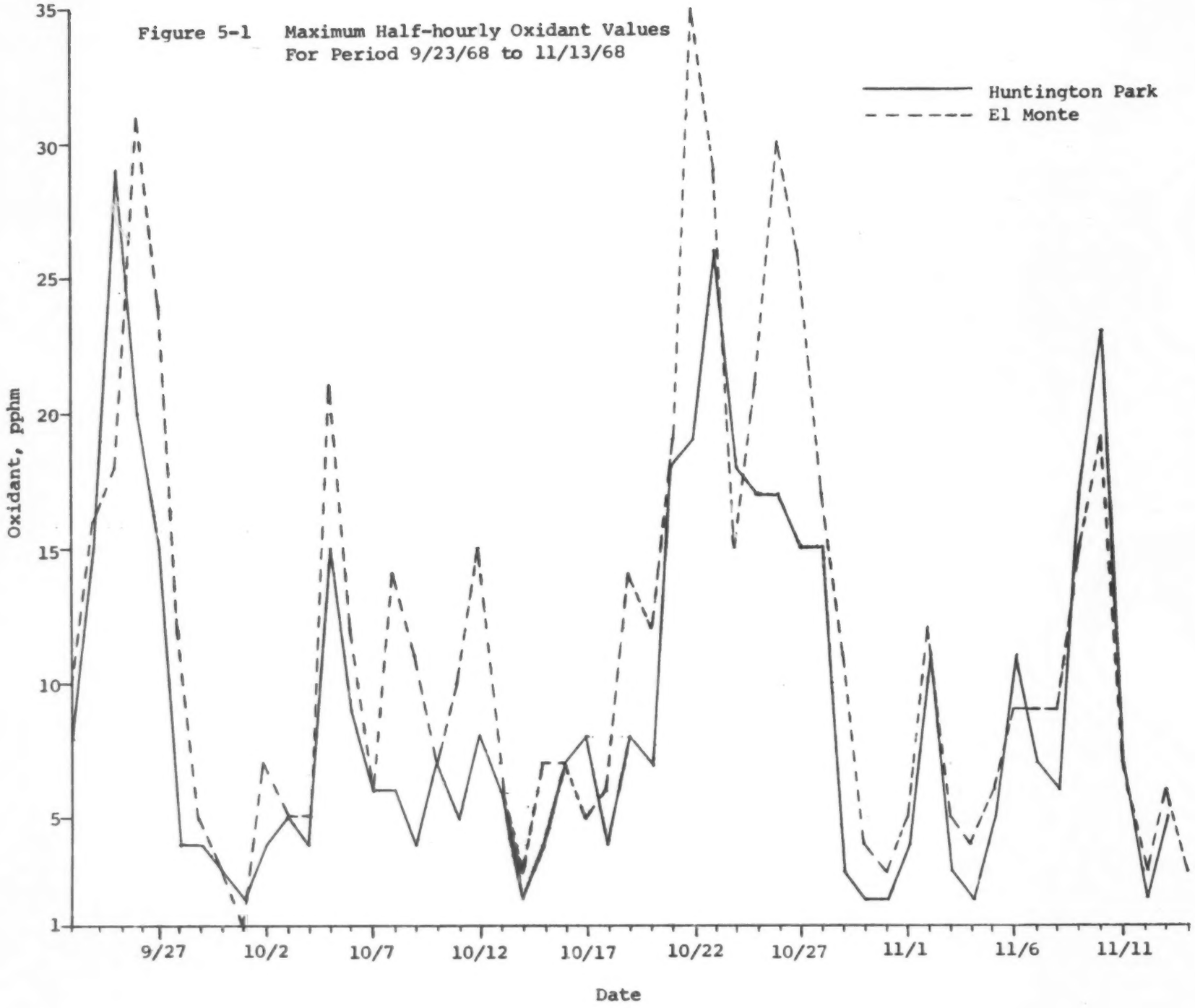


Figure 5-2 Time of Oxidant Maxima

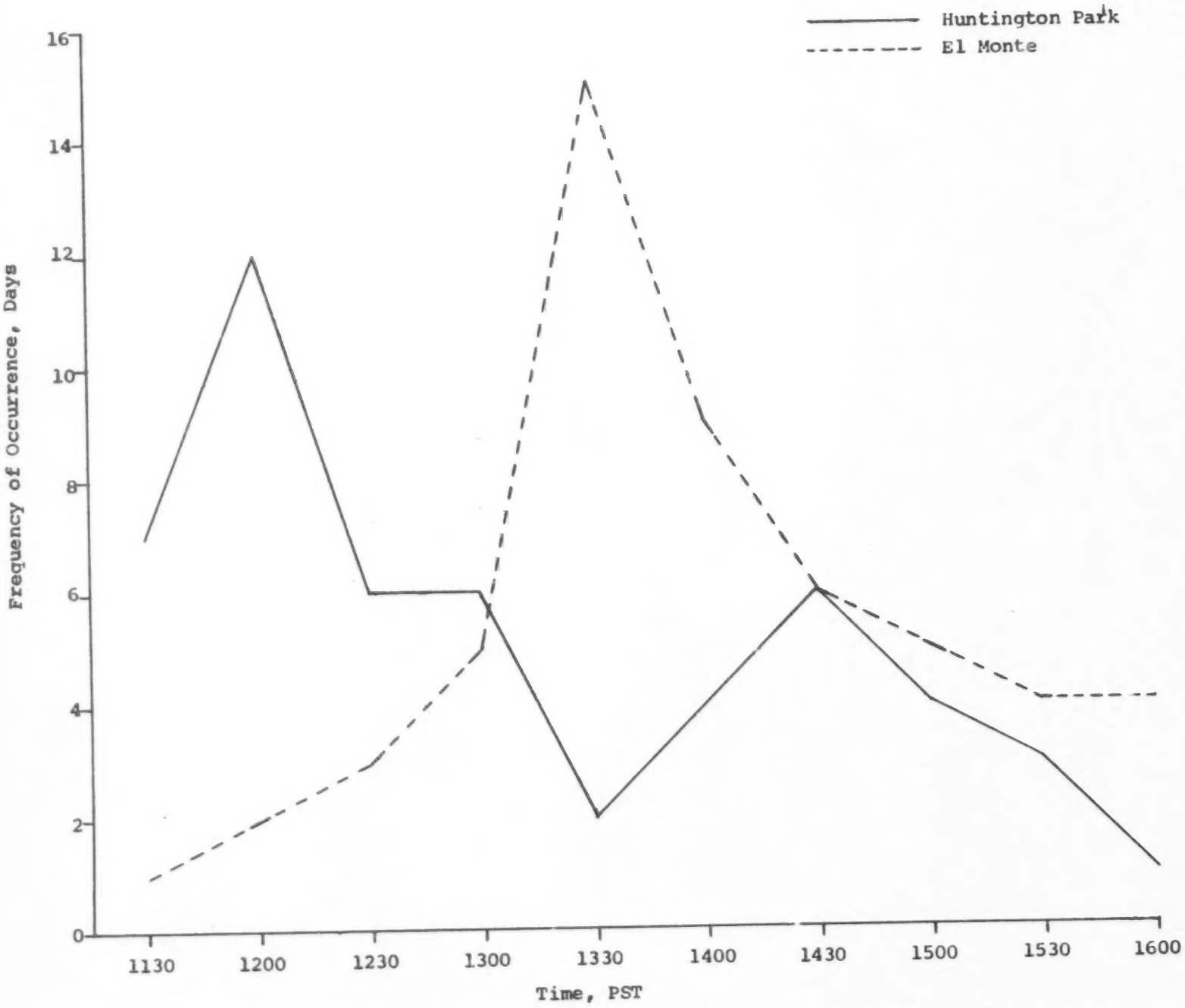


Figure 5-4 Diurnal Pattern of Pollutants and Wind Speed

El Monte

October 18, 1968

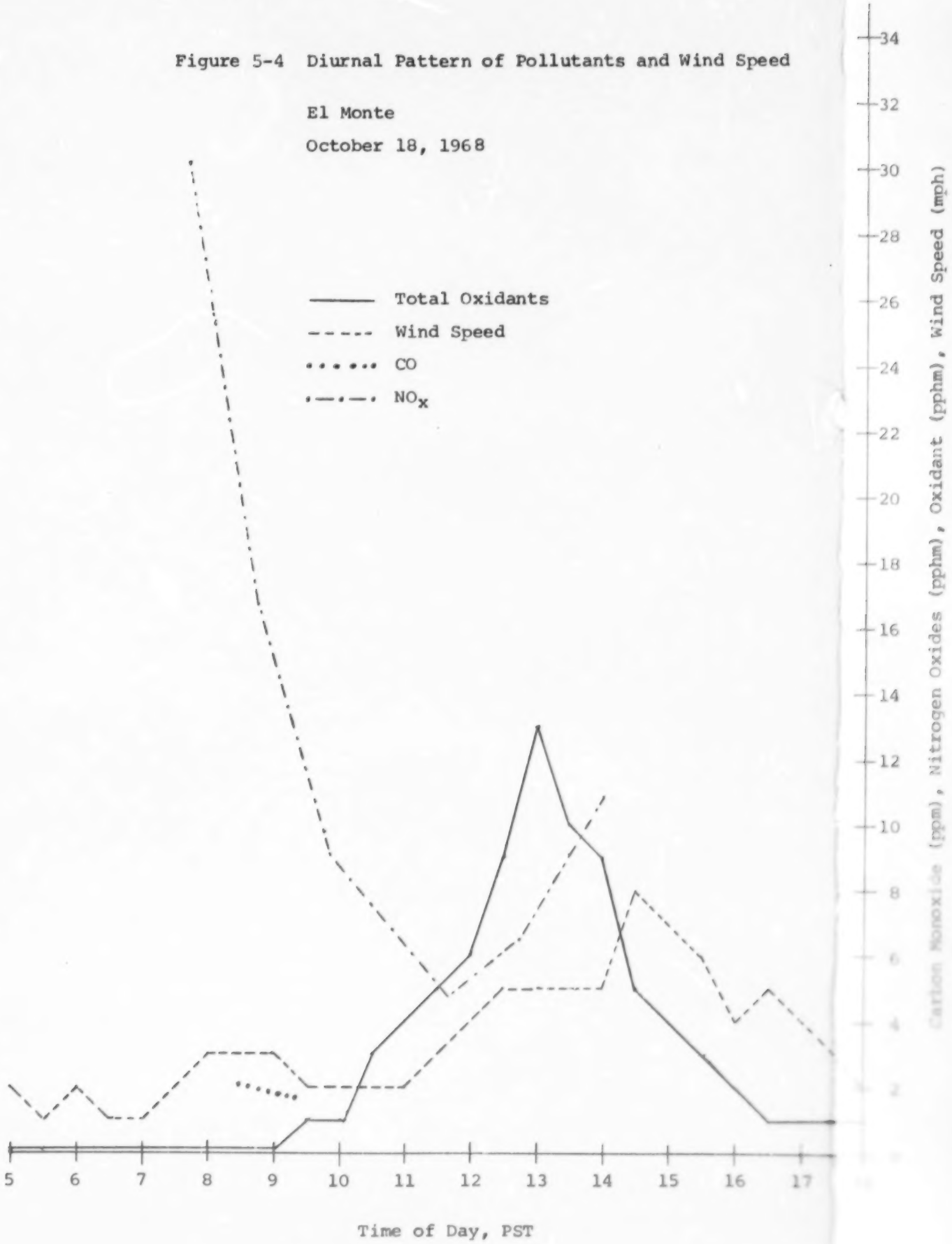


Figure 5-3 The Relationship Between Daily Maximum Oxidant and Maximum Temperature

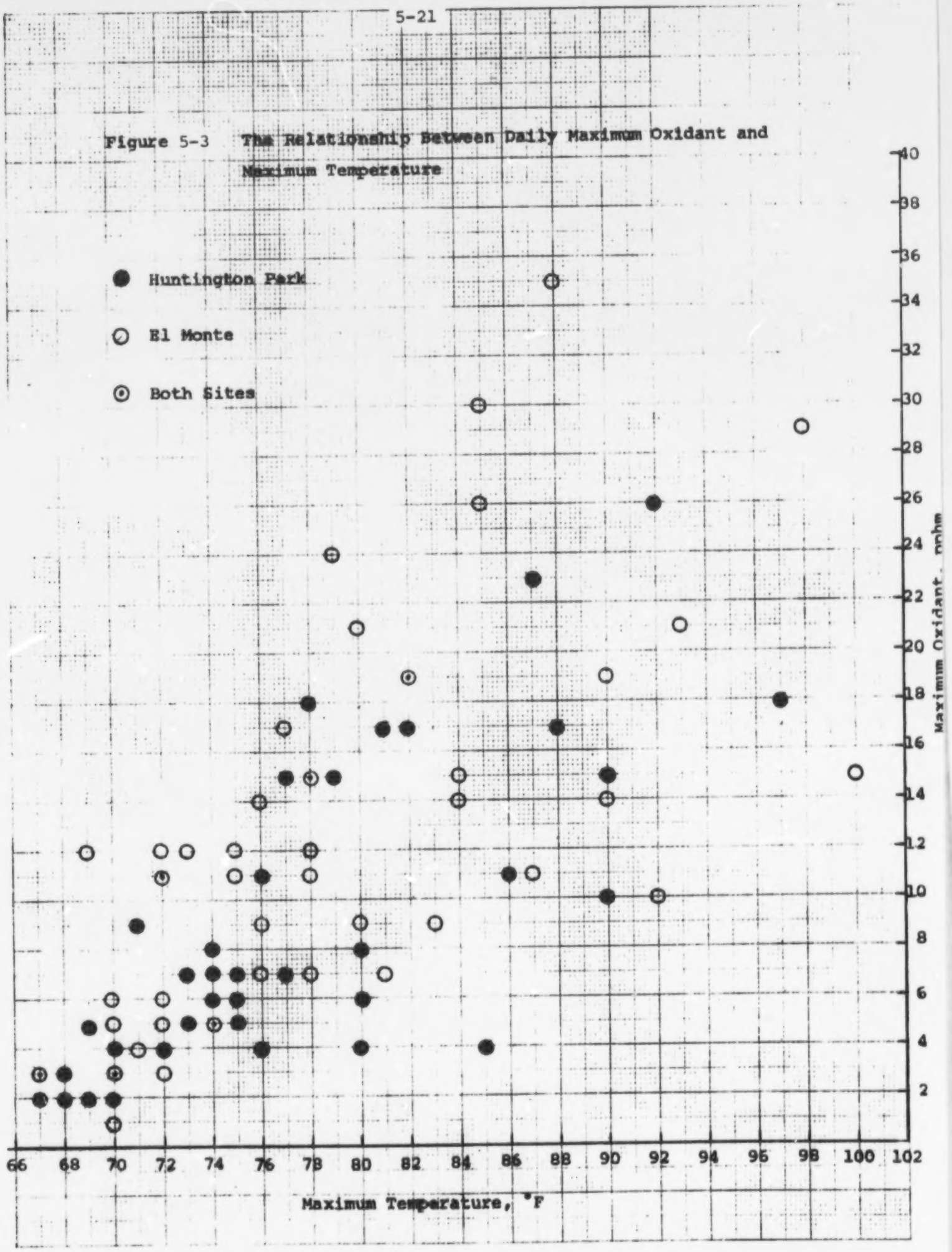


Figure 5-5 Diurnal Pattern of Pollutants and Wind Speed

Huntington Park

October 18, 1968

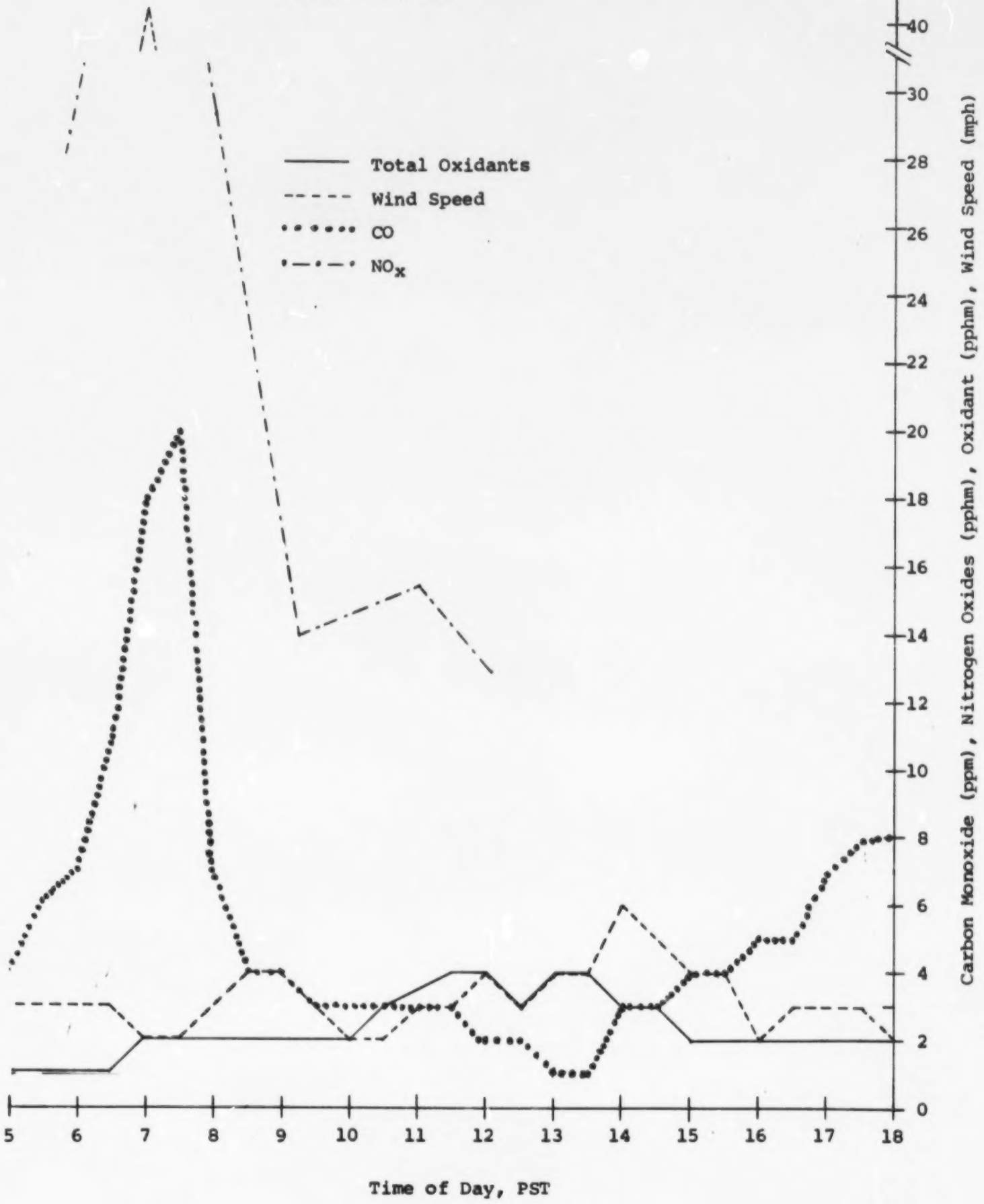


Figure 5-6 Diurnal Pattern of Pollutants and Wind Speed

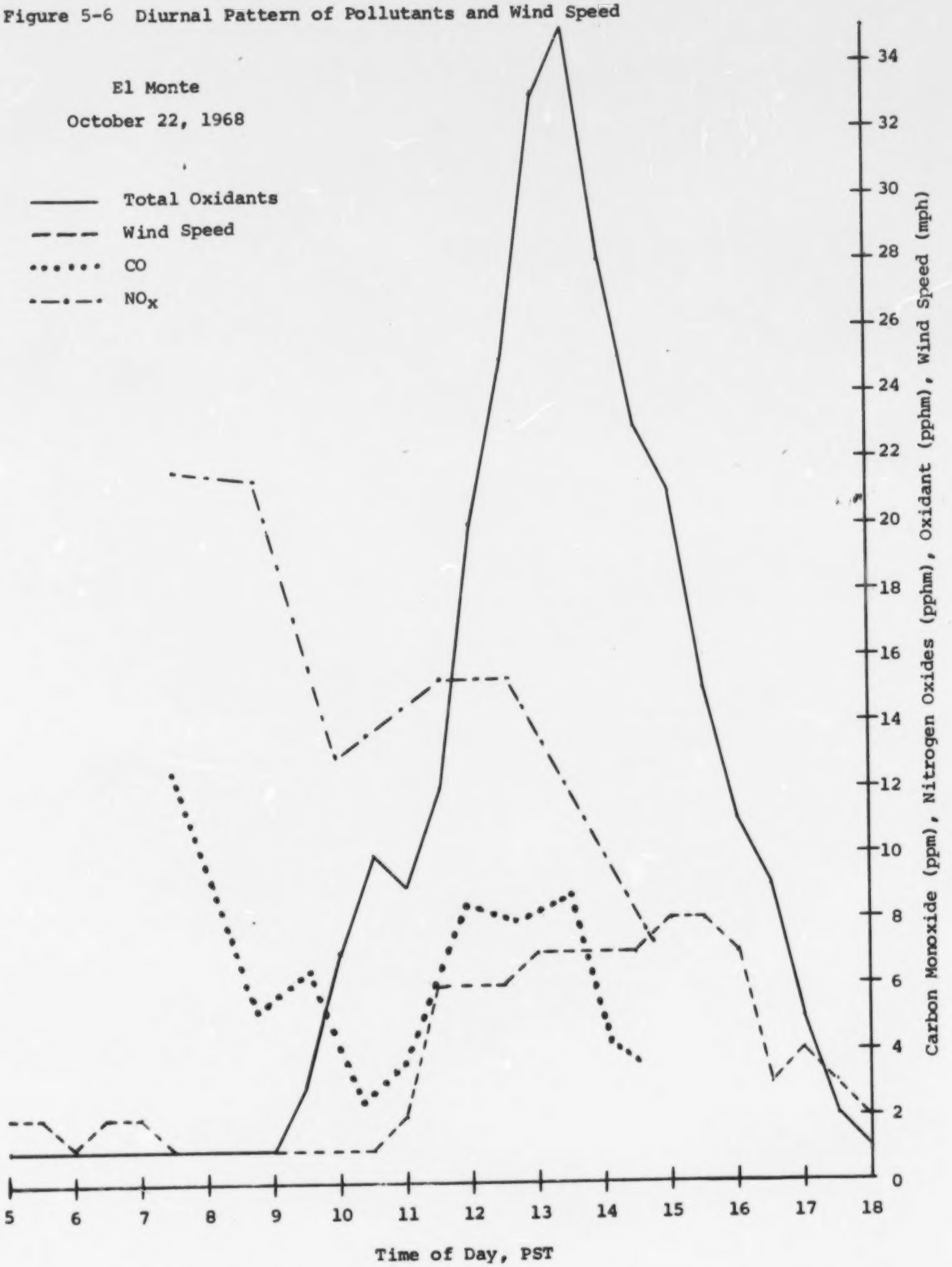


Figure 5-7 Diurnal Pattern of Pollutants and Wind Speed
Huntington Park
October 22, 1968

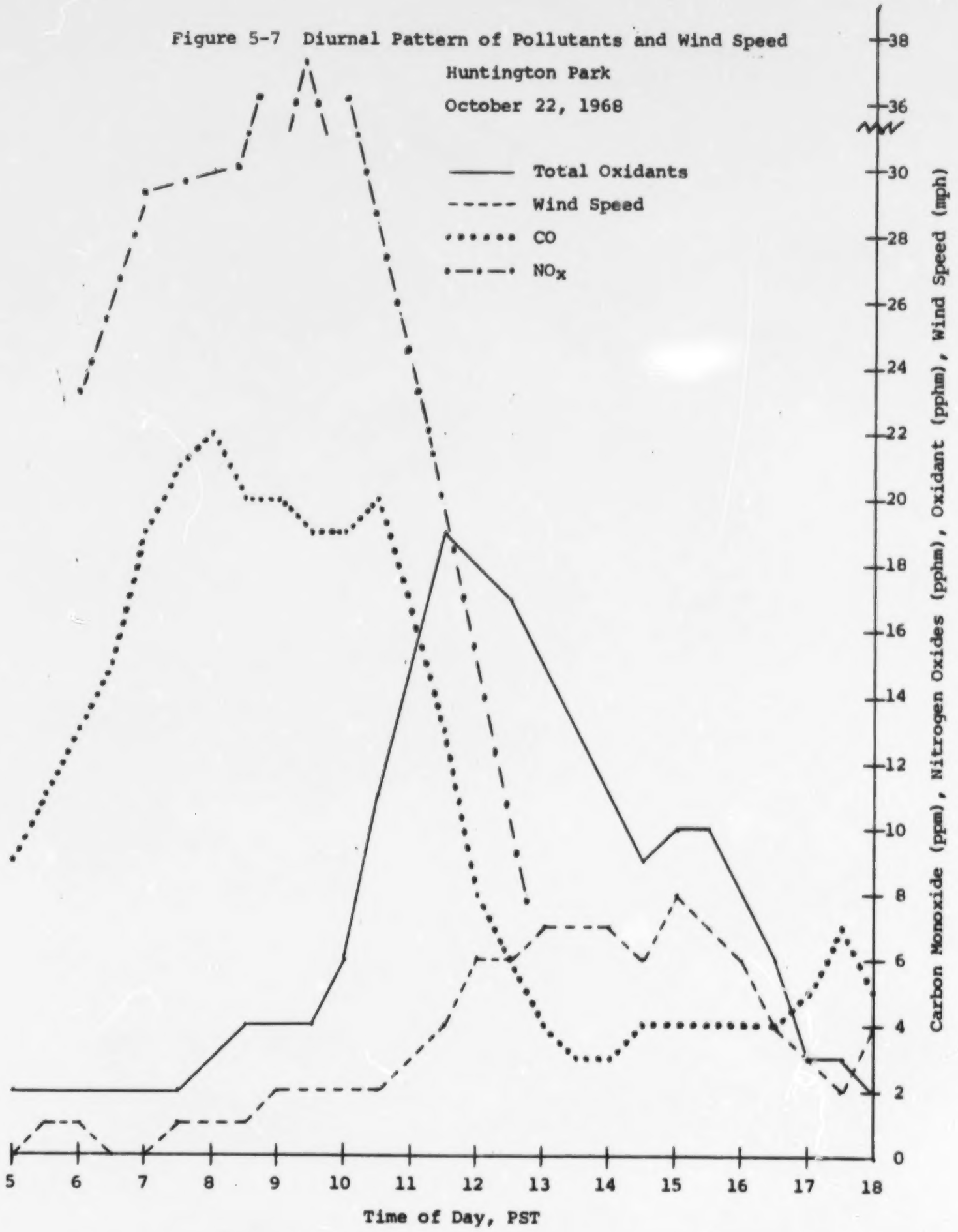


Figure 5-8 Diurnal Pattern of Pollutants and Wind Speed

El Monte

October 23, 1968

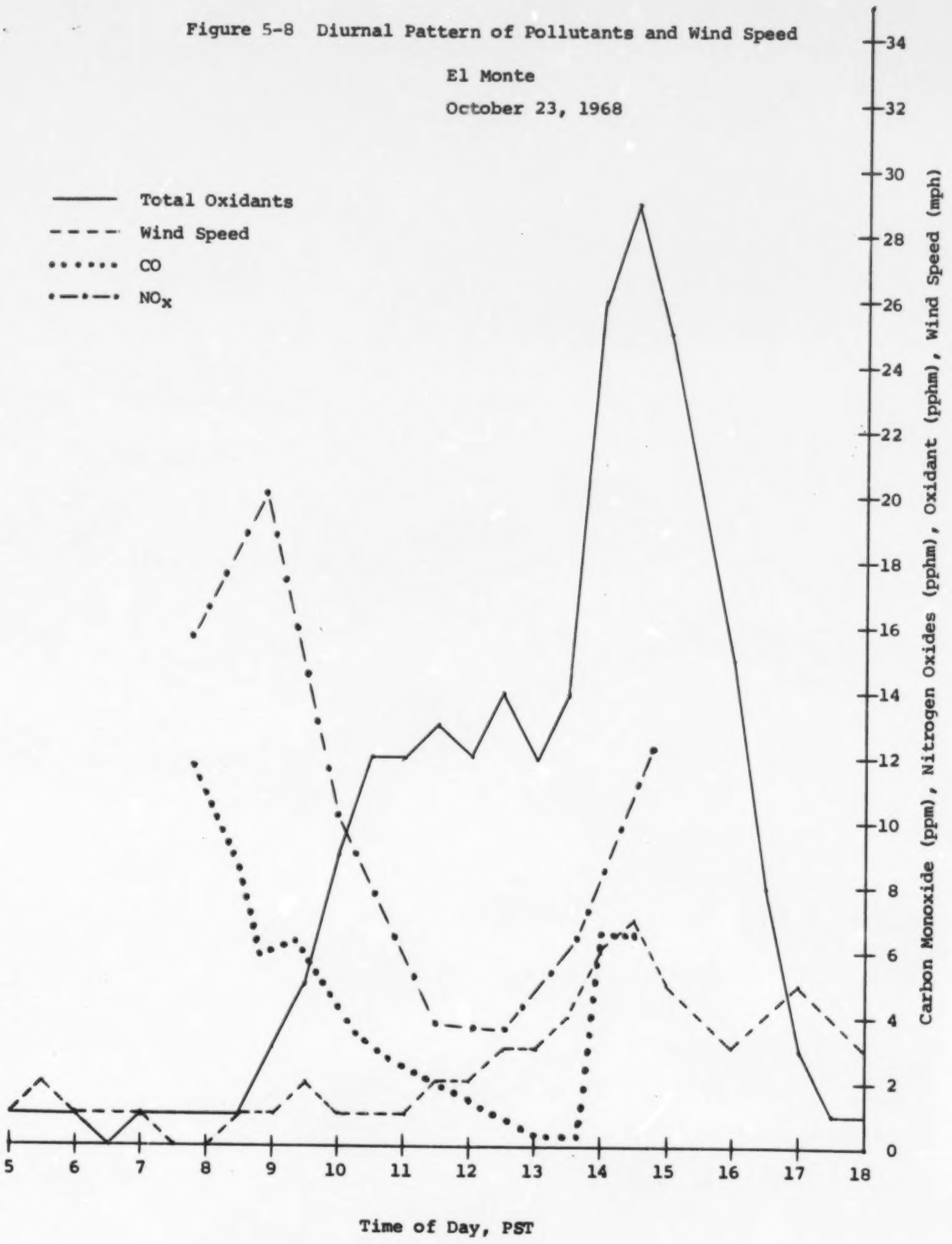


Figure 5-9 Diurnal Pattern of Pollutants and Wind Speed

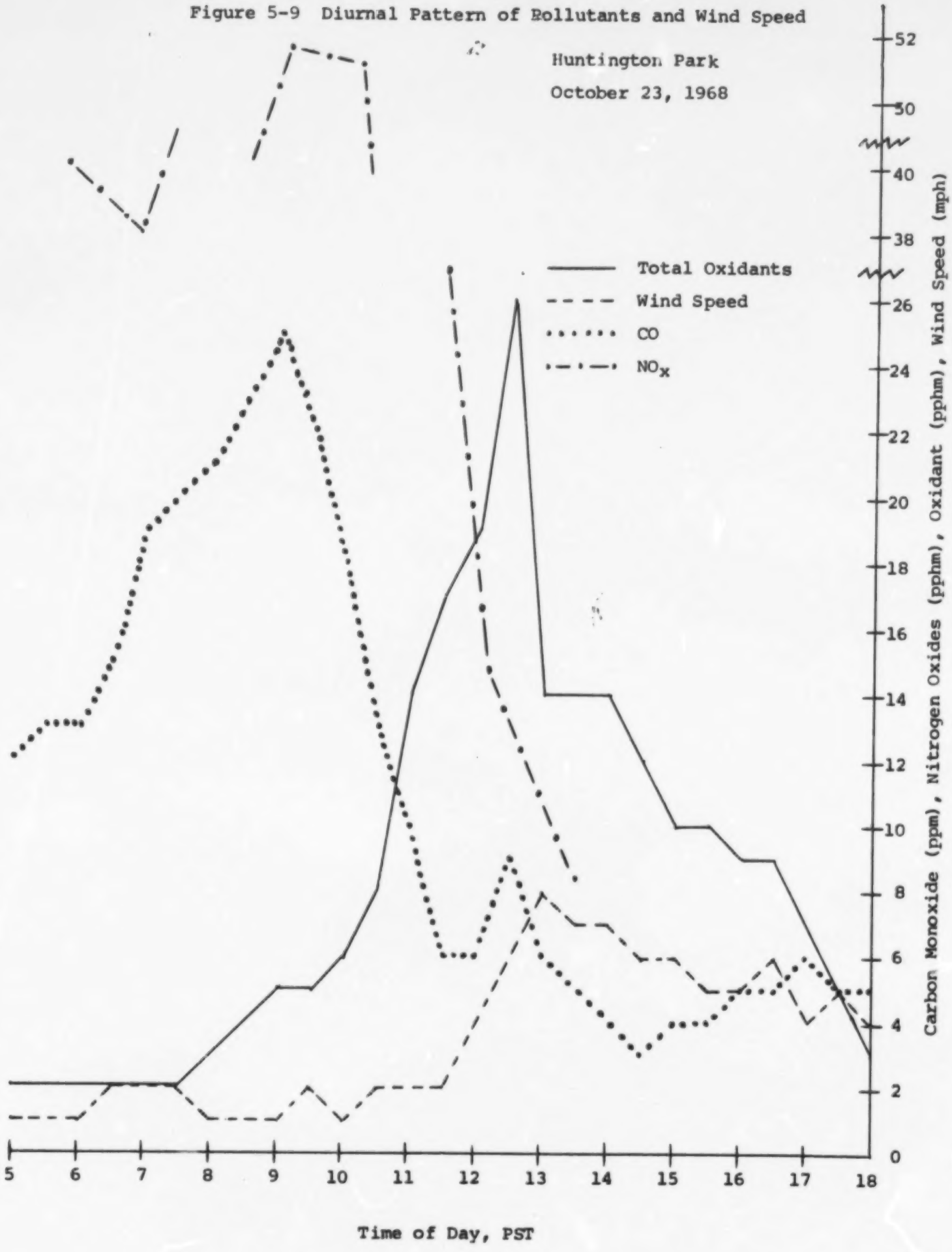


Figure 5-10 Diurnal Pattern of Pollutants and Wind Speed

El Monte

October 24, 1968

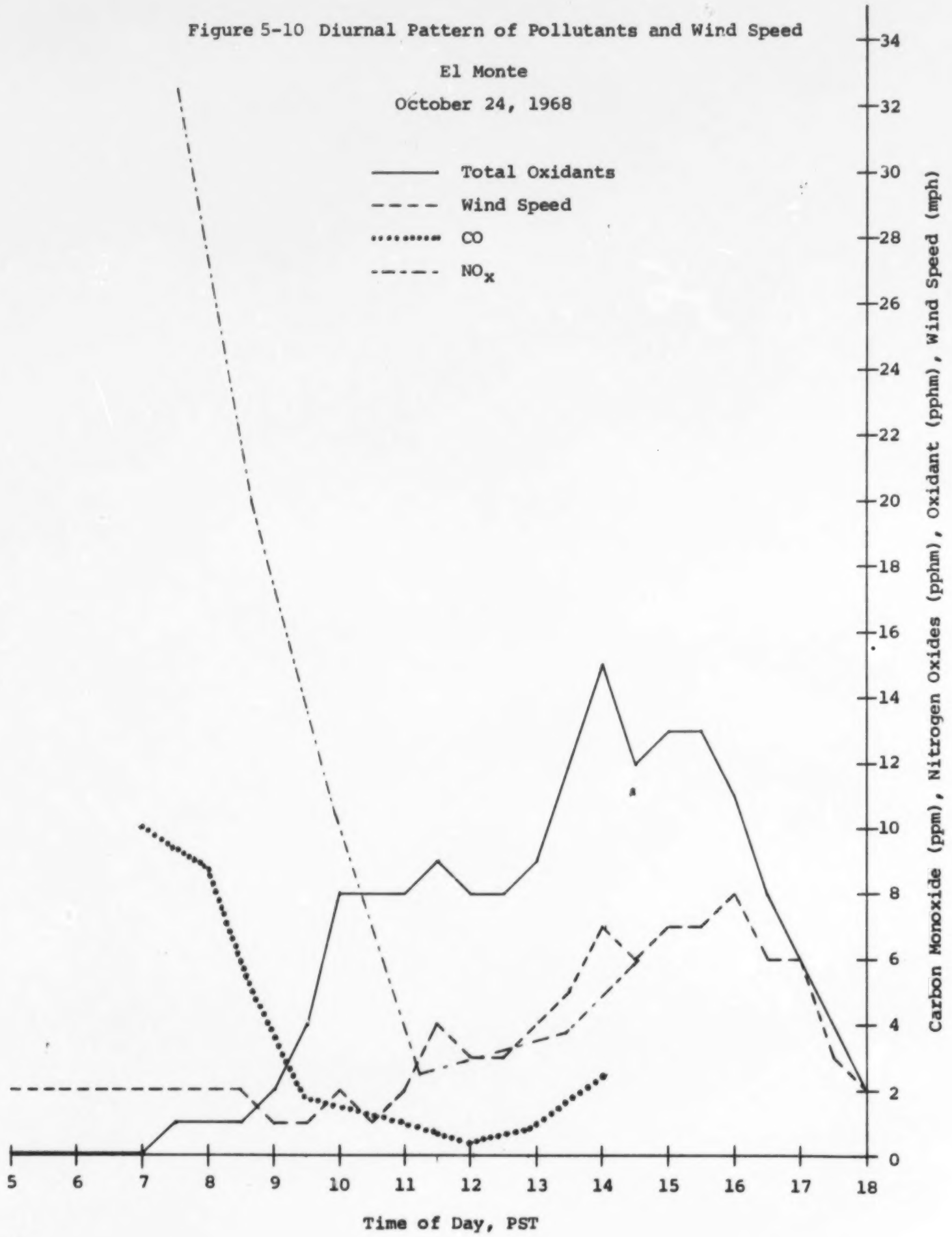


Figure 5-11 Diurnal Pattern of Pollutants and Wind Speed

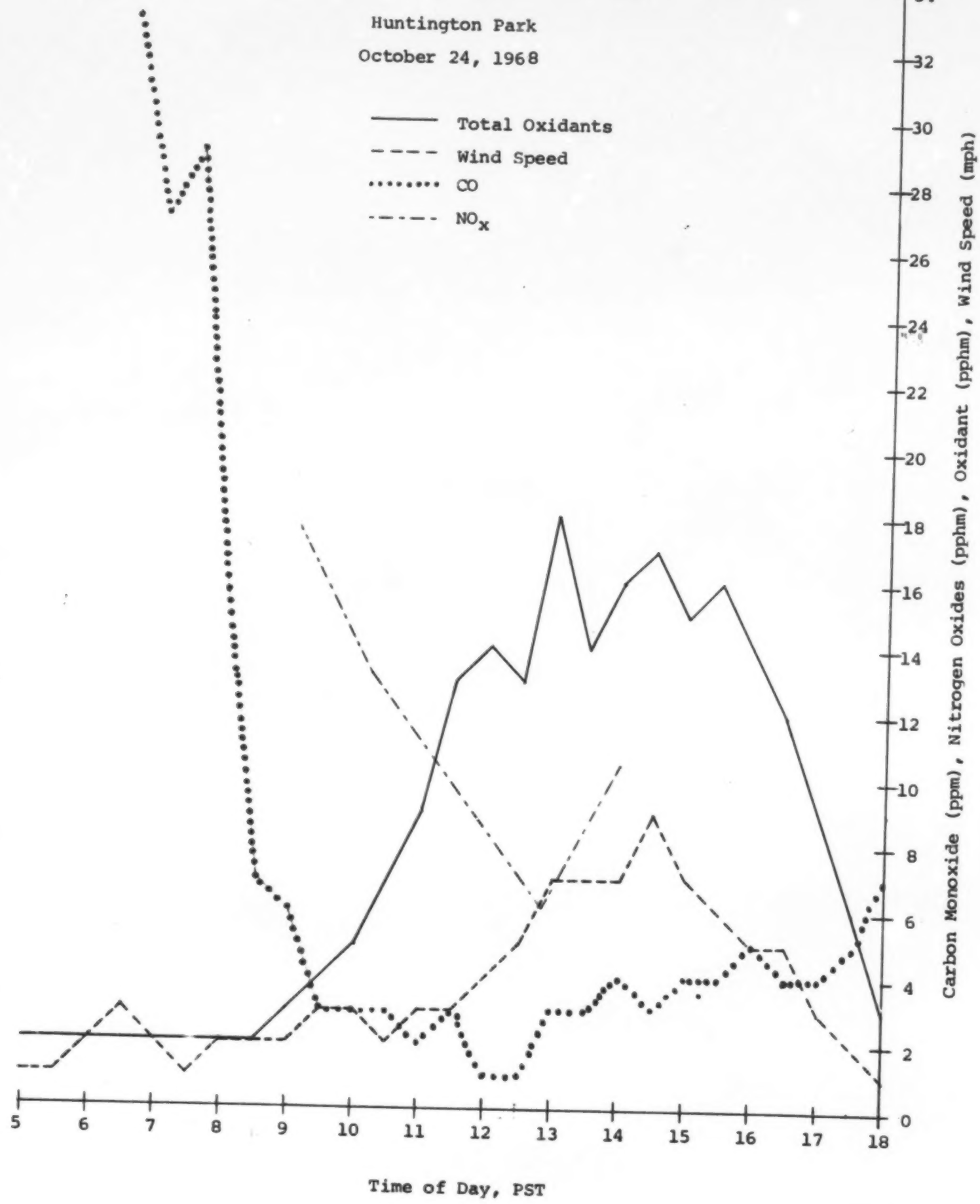


Figure 5-12 Diurnal Pattern of Pollutants and Wind Speed

El Monte

October 28, 1968

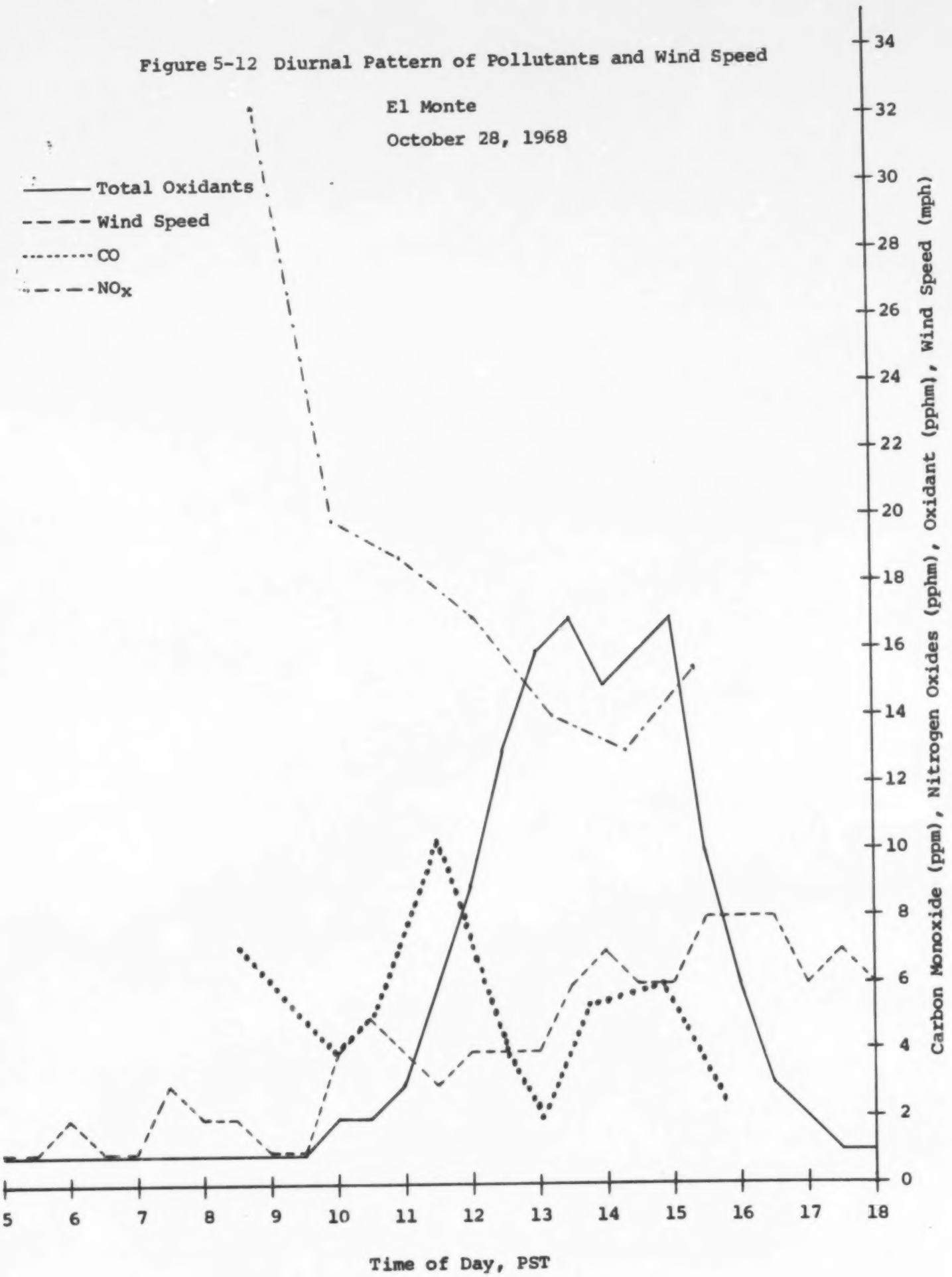


Figure 5-13 Diurnal Pattern of Pollutants and Wind Speed

Huntington Park

October 28, 1968

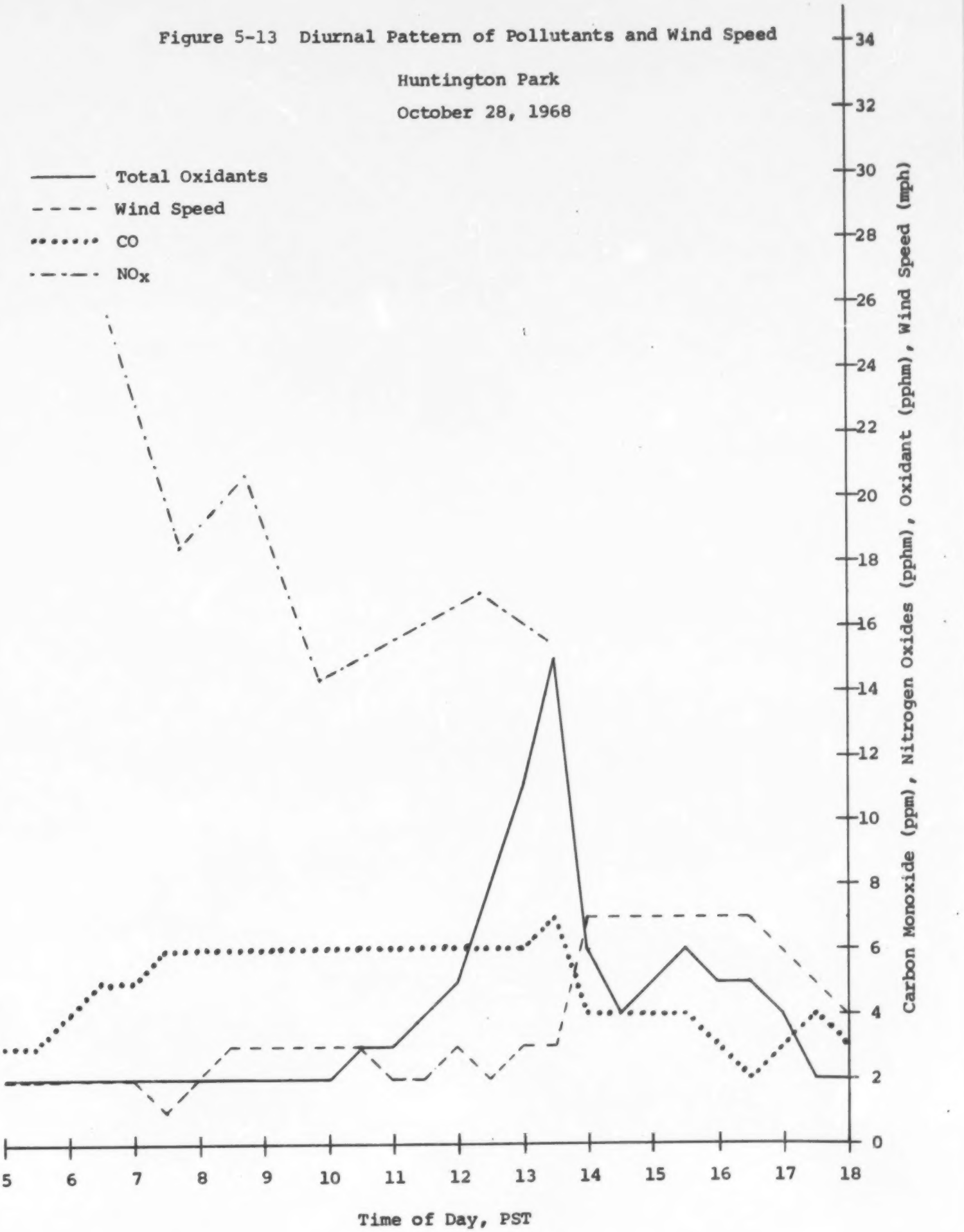


Table 5-1

HALF-HOURLY AVERAGES OF ELEMENTS MEASURED CONTINUOUSLY AT EL MONTE, CALIF. October 22 and 23, 1968

PST

Day	0000		0100		0200		0300		0400	
Total Oxidants (pphm)										
22	1	1	1	1	1	1	1	1	1	1
23	1	1	1	1	1	1	1	1	1	1
Wind Speed (mph)										
22	2	1	1	2	2	1	1	2	1	1
23	1	2	1	1	1	2	1	0	1	1
Wind Direction (deg)										
22	50	90	45	50	25	310	25	55	70	55
23	10	40	130	55	335	30	50	200	55	50
Relative Humidity (%)										
22	97		97		97		97		97	
23	98		98		98		98		98	
Temperature (^{o}F)										
22	56		55		54		53		52	
23	56		55		53		53		52	
Ozone (pphm)										
UV Radiation (watts per m^{2})										

Day	0500		0600		0700		0800		0900	
Total Oxidants										
22	1	1	1	1	1	1	1	1	1	3
23	1	1	1	0	1	1	1	1	3	5
Wind Speed										
22	2	2	1	2	2	1	1	1	1	1
23	1	2	1	1	1	0	0	1	1	2
Wind Direction										
22	50	30	40	15	30	30	215	120	150	320
23	50	35	25	45	35	20	350	265	55	120
Relative Humidity										
22	97		97		97		84		50	
23	98		98		93		70		46	
Temperature										
22	52		51		51		60		72	
23	51		50		51		61		71	
Ozone (pphm)										
UV Radiation										
22						6.7	9.4	12.4	13.8	16.8
23										

Day	1000		1100		1200		1300		1400	
Total Oxidants										
22	7	10	9	12	20	25	33	35	28	23
23	9	12	12	13	12	14	12	14	26	29
Wind Speed										
22	1	1	2	6	6	6	7	7	7	7
23	1	1	1	2	2	3	3	4	6	7
Wind Direction										
22	245	270	255	225	215	225	220	230	240	245
23	45	55	350	210	255	240	255	250	245	220
Relative Humidity										
22	35		24		18		24		25	
23	30		28		11		10		8	
Temperature										
22	78		88		87		88		88	
23	80		90		95		98		97	
Ozone										
22			8	10	16	21	28	30	24	20
23			10	12	10	12	10	12	23	25
UV Radiation										
22	19.5	20.2	21.5	20.8	25.2	23.5	18.5	21.2	21.8	22.2
23	19.0	20.2	21.8	22.9	21.5	20.2	19.8	16.8	10.1	9.1

Day	1500		1600		1700		1800		1900	
Total Oxidants										
22	21	15	11	9	5	2	1	1	1	1
23	25	20	15	8	3	1	1	1	1	1
Wind Speed										
22	8	8	7	3	4	3	2	3	2	1
23	5	4	3	4	5	4	3	1	0	0
Wind Direction										
22	230	240	225	255						145
23	230	240	230	200	205	200	195	110	5	15
Relative Humidity										
22	26		29		33		45		60	
23	18		15		18		24		40	
Temperature										
22	86		81		76		70		66	
23	95		95		88		78		72	
Ozone										
22	18	13								
23	21	16	12	5						
UV Radiation										
22	20.8									
23	7.7	4.7	3.0							

Day	2000		2100		2200		2300	
Total Oxidants								
22	1	1	1	1	1	1	1	1
23	1	1	1	1	1	1	1	1
Wind Speed								
22	1	1	2	1	1	1	1	1
23	1	1	1	2	1	1	2	1
Wind Direction								
22	130	150	115	215	185	60	135	20
23	160	240	210	200	75	15	25	310
Relative Humidity								
22	74		88		97		98	
23	52		66		80		86	
Temperature								
22	64		60		58		58	
23	68		64		63		60	
Ozone								
UV Radiation								

CONCENTRATIONS OF VARIOUS POLLUTANTS IN ATMOSPHERE AT EL MONTE, CALIF., pphm

Date 1968	Time PST	Aliphatic Aldehydes	Formal-dehyde	Acrolein	Nitrogen Dioxide	Nitric Oxide	Total Nitrogen Oxides
10/22	0738	6.8	2.5	0.2	9.8	12.0	21.8
	0850	9.0	3.5	0.3	16.6	4.9	21.5
	0956	7.4	3.3	0.3	11.9	1.2	13.1
	1130	5.5	4.9	0.4	13.8	1.6	15.4
	1235	12.0	8.9	0.8	14.2	1.1	15.3
	1338	14.8	9.0	0.8	10.4	0.8	11.2
	1442	8.4	-	-	6.9	0.4	7.3
10/23	0745	-	-	0.4	3.5	12.2	15.7
	0850	9.5	4.0	0.3	14.6	5.5	20.1
	1000	7.7	4.8	0.4	8.6	1.6	10.2
	1130	4.9	3.1	0.1	2.8	1.0	3.8
	1235	4.1	1.9	0.2	2.7	0.9	3.6
	1340	4.3	2.8	0.5	5.8	0.7	6.5
	1445	-	-	0.6	11.8	0.5	12.3

CONCENTRATION OF CARBON MONOXIDE AT GROUND LEVEL

Date 1968	Time PST	El Monte Carbon Monoxide (ppm)
22 Oct.	0725	12.6
	0818	7.6
	0845	5.5
	0935	6.3
	1020	2.5
	1101	3.8
	1155	8.4
	1240	8.0
	1330	8.8
	1406	4.2
	1430	3.8
23 Oct.	0742	11.7
	0820	8.6
	0842	5.9
	0915	6.3
	1012	3.5
	1042	2.7
	1210	1.0
	1255	0.5
	1335	0.5
	1355	6.6
	1430	6.6

Table 5-2

HALF-HOURLY AVERAGES OF ELEMENTS MEASURED CONTINUOUSLY AT HUNTINGTON PARK, CALIF.
October 22 and 23, 1968

PST

Day	0000		0100		0200		0300		0400	
Total Oxidants (pphm)										
22	2	1	1	1	1	2	2	2	2	2
23	2	2	2	2	2	2	2	2	2	2
Carbon Monoxide (ppm)										
22	6	5	4	4	3	4	5	6	7	9
23	8	9	9	9	9	9	9	10	10	11
Total Hydrocarbons (ppm)										
22	11	11	11	11	11	11	11	10	10	9
23	10	10	10	10	10	9	9	9	9	9
Wind Speed (mph)										
22	1	2	2	2	3	3	1	1	1	0
23	1	1	1	1	1	2	1	1	1	1
Wind Direction (deg)										
22	15	200	240	290	295	320	05	00	15	70
23	15	255	310	235	345	120	60	05	10	30
Relative Humidity (%)										
22	92		98		98		98		98	
23	95		95		95		95		95	
Temperature (^{o}F)										
22	54		55		56		54		52	
23	54		53		52		52		52	
Ozone (pphm)										

Day	0500		0600		0700		0800		0900	
Total Oxidants										
22	2	2	2	2	2	2	3	4	4	4
23	2	2	2	2	2	2	3	4	5	5
Carbon Monoxide										
22	9	11	13	15	19	21	22	20	20	19
23	12	13	13	16	19	20	21	23	25	22
Total Hydrocarbons										
22	9	10	9	9	9	9	9	9	9	9
23	9	9	9	9	9	9	8	8	8	8
Wind Speed										
22	0	1	1	0	0	1	1	1	2	2
23	1	1	1	2	2	2	1	1	1	2
Wind Direction										
22	75	30	255	00	15	95	145	200	210	255
23	95	165	265	305	260	265	305	10		
Relative Humidity										
22	97		97		97		74		54	
23	95		95		95		85		45	
Temperature										
22	51		50		51		56		63	
23	52		52		52		57		64	
Ozone										

Day	1000		1100		1200		1300		1400	
Total Oxidants										
22	6	11	15	19	18	17	15	13	11	9
23	6	8	14	17	19	26	14	14	14	12
Carbon Monoxide										
22	19	20	17	13	8	6	4	3	3	4
23	18	13	10	6	6	9	6	5	4	3
Total Hydrocarbons										
22	9	9	9	9	11	11	9	7	6	6
23	9	10	10	10	10	11	11	10	8	8
Wind Speed										
22	2	2	3	4	6	6	7	7	7	6
23	1	2	2	2	4	6	8	7	7	6
Wind Direction										
22	215	195	190	215	235	250	260	260	260	265
23	20	320	285	290	260	245	250	265	275	275
Relative Humidity										
22	32		18		18		18		20	
23	12		5		2		18		14	
Temperature										
22	72		79		82		80		79	
23	80		87		92		83		84	
Ozone										
22		5	8	12	12	11	10	8	7	5
23		2	8	11	13	18	9	9	9	8

Day	1500		1600		1700		1800		1900	
Total Oxidants										
22	10	10	8	6	3	3	2	2	2	2
23	10	10	9	9	7	5	3	3	2	2
Carbon Monoxide										
22	4	4	4	4	5	7	5	4	3	3
23	4	4	5	5	6	5	5	5	5	4
Total Hydrocarbons										
22	7	7	6	7	7	9	9	7	6	6
23	8	8	8	8	8	8	8	9	8	9
Wind Speed										
22	8	7	6	4	3	2	4	4	3	3
23	6	5	5	6	4	5	4	2	2	2
Wind Direction										
22	260	265	260	250	235	230	220	250	265	240
23	265	255	255	255	260	270	260	240	205	270
Relative Humidity										
22	22		29		40		70		85	
23	14		16		22		55		74	
Temperature										
22	77		73		69		63		59	
23	85		81		73		66		63	
Ozone										
22	6	6	4	2						
23	6	6	5	5						

Day	2000		2100		2200		2300	
Total Oxidants								
22	2	2	2	2	2	2	2	2
23	2	2	2	2	2	2	2	2
Carbon Monoxide								
22	4	4	4	4	5	5	6	7
23	4	5	7	8				
Total Hydrocarbons								
22	7	7	8	8	9	11	11	11
23	8	9	10	11				
Wind Speed								
22	2	2	2	1	1	0	1	1
23	2	1	1	0	2	2	3	2
Wind Direction								
22	230	210	255	335	350	00	05	35
23	285	305	05	10	05	00		15
Relative Humidity								
22	88		95		95		95	
23	80		84		86		78	
Temperature								
22	57		57		57		56	
23	62		60		58		58	
Ozone								

CONCENTRATIONS OF VARIOUS POLLUTANTS IN ATMOSPHERE AT HUNTINGTON PARK, CALIF., pphm

Date 1968	Time PST	Aliphatic Aldehydes	Formal-dehyde	Acrolein	Nitrogen Dioxide	Nitric Oxide	Total Nitrogen Oxides
10/22	0555	4.3	2.3	0.3	10.1	13.2	23.3
	0658	5.9	2.6	0.3	12.1	17.2	29.3
	0815	8.0	5.7	0.5	19.8	10.4	30.2
	0921	13.9	10.0	0.6	28.1	9.3	37.4
	1115	16.4	13.6	1.1	19.5	2.6	22.1
	1240	8.8	8.1	0.7	6.7	1.1	7.8
10/23	0545	--	2.7	0.4	10.6	29.5	40.1
	0647	3.9	2.4	0.3	11.3	26.7	38.0
	0904	--	7.6	0.8	33.4	18.4	51.8
	1010	17.3	9.7	1.0	45.9	5.3	51.2
	1208	12.2	9.1	0.8	12.6	2.2	14.8
	1330	--	5.0	0.6	7.8	0.6	8.4

Table 5-3

Hydrocarbon Concentrations at Huntington Park

October 22, 1968, ppb

Peak No.	Compound	Ground Level 1325 PST	Ground Level 0800 PST	at 1,500 ft. 0743 PST	at 2,200 ft. 0807 PST
--	Methane	2030	5980	1720	1610
--	Ethane	79	406	43	39
--	Ethylene	11	139	< 3	< 3
--	Acetylene	29	192	13	4
--	Propane	23	166	13	9
--	Propylene	10	45	4	8
--	Isobutane	6	34	5	< 3
--	Butane	29	165	8	3
--	Butenes	5	8	< 3	< 3
1	Isopentane	19.3	115	7.7	3.0
2	1-Pentene + 2 Methyl-1-Butene	0.1	1.4	< 0.1	< 0.1
3	n-Pentane	9.1	62.9	2.6	1.1
4	trans-2-Pentene	nd	2.8	nd	nd
5	cis-2-Pentene	< 0.1	0.8	nd	nd
6	2-Methyl-2-butene	< 0.1	4.2	nd	nd
7	2,2-Dimethylbutane	< 0.1	0.6	0.2	0.1
8		nd	< 0.1	nd	nd
9		nd	< 0.1	nd	nd
10	Cyclopentene	< 0.1	0.7	nd	nd
11	Cyclopentane	0.6	7.2	0.2	0.1
12	2,3-Dimethylbutane	0.6	7.8	2.1	0.1
13	2-Methylpentane	4.3	32.7	5.2	0.7
14	3-Methylpentane	2.9	22.2	3.2	0.4
15	1-Hexene	0.2	2.5	nd	nd
16	n-Hexane	3.4	28.4	2.0	0.5
17	trans-3-Hexene	< 0.1	2.2	nd	nd
18	trans-2-Hexene	< 0.1	2.5	nd	nd
19	cis-3-Hexene	nd	0.2	nd	nd
20	cis-2-Hexene	nd	nd	nd	nd
21	Methylcyclopentane	3.7	28.1	1.6	0.1
22	2,4-Dimethylpentane	----	13.4	1.9	0.1
23		----	23.6	----	----
24		----	----	----	----
25		0.1	0.5	----	0.1
26	Benzene + Cyclohexane	5.2	32.1	2.2	0.9
27	2-Methylhexane + 2,3-Dimethylpentane	3.2	20.1	3.6	0.9
28	3-Methylhexane	1.6	11.6	0.4	0.1
29		4.0	5.9	0.1	< 0.1
30		3.5	5.3	0.1	< 0.1
31		1.1	8.4	----	----
32	2,2,4-Trimethylpentane	1.1	10.2	18.9	----
33	1-Heptene + ?	2.0	5.0	2.2	----
34	n-Heptane	2.8	15.0	3.0	0.2
35		nd	< 0.1	nd	nd

Hydrocarbon Concentrations at Huntington Park

October 22, 1968, ppb

Peak No.	Compound	Ground Level 1325 PST	Ground Level 0800 PST	at 1,500 ft. 0743 PST	at 2,200 ft. 0807 PST
36		< 0.1	0.1	nd	nd
37	Methylcyclohexane	3.5	15.6	0.3	0.1
38		0.3	2.2	0.2	0.1
39		0.6	4.2	0.2	0.1
40	2,4-Dimethylhexane	0.3	3.5	6.4	0.4
41	2,5-Dimethylhexane	0.2	3.0	3.4	0.3
42		0.3	2.3	0.1	< 0.1
43		0.2	1.7	0.1	nd
44		0.5	3.8	10.7	0.6
45	2,3,4-Trimethylpentane	0.5	4.5	13.7	0.5
46	Toluene	13.1	77.4	64.2	14.4
47		0.7	9.4	6.0	0.3
48		0.7	10.4	4.6	0.3
49		nd	0.1	nd	nd
50		0.7	3.4	9.8	0.5
51		0.1	0.4	0.2	< 0.1
52		0.9	1.3	1.2	1.2
53	n-Octane	1.4	10.4	3.3	0.4
54		nd	0.2	0.2	
55		0.1	1.4	< 0.1	
56		0.1	0.5	1.5	
57		0.1	1.1	0.4	
58		5.2	4.0	1.0	
59		0.2	6.3	1.3	
60		< 0.1	1.1	nd	
61	Ethylbenzene	1.5	16.7	12.2	3.0
62		0.1	1.0	----	
63		nd	0.2	0.1	
64	m + p-Xylene	5.4	43.8	46.0	8.5
65		0.1	1.4	0.3	
66		0.2	0.4	0.9	
67		2.3	1.7	----	
68	o-Xylene	2.3	17.9	9.8	2.4
69		0.7	0.4	0.9	1.0
70		nd	0.2		
71	n-Nonane	0.5	6.7	0.2	< 0.1
72		< 0.1	0.7		
73		< 0.1	0.6		
74	Isopropylbenzene	0.1	1.3	0.2	< 0.1
75		< 0.1	0.3		
76		0.1	1.2		
77		0.3	0.9		
78		0.2	1.6		
79		0.2	1.3		
80	n-Propylbenzene	0.3	2.3	0.2	0.1

Hydrocarbon Concentrations at Huntington Park

October 22, 1968, ppb

Peak No.	Compound	Ground Level 1325 PST	Ground Level 0800 PST	at 1,500 ft. 0743 PST	at 2,200 ft. 0807 PST
81	4-Ethyltoluene	1.4	11.2	0.4	0.3
82	3-Ethyltoluene	0.6	5.2	0.2	0.2
83		0.2	2.9	1.0	0.4
84	1,3,5-Trimethylbenzene	0.3	6.2	0.2	0.1
85	2-Ethyltoluene		5.0	0.3	0.1
86		----	----	0.2	nd
87	tert-Butylbenzene	0.1	2.2	0.2	< 0.1
88	1,2,4-Trimethylbenzene	1.7	18.9	1.1	0.6
89	n-Decane	0.8	4.5	0.4	0.3
90	sec-Butylbenzene	----	----		
91	Isobutylbenzene	nd	----		
92		< 0.1	0.4		
93		0.8	3.4	0.2	0.1
94		< 0.1	1.2		
95		0.1	2.5		
96		nd	0.1		
97		nd	0.6		
98		nd	0.3		
99		0.1	1.2		
100		0.1	1.0		
101	n-Butylbenzene	0.2	1.6		
102		< 0.1	0.2		
103		< 0.1	0.3		
104		< 0.1	0.3		
105		< 0.1	1.3		
106		< 0.1	1.6		
107	n-Undecane	0.1	3.2		
108		nd	0.3		
109		1.4	3.0		
	Other Pollutants				
	Carbon Monoxide, ppm	3	22	< 0.5	< 0.5
	Nitrogen Dioxide, pphm	6.7*	19.8	0.8	< 0.2
	Nitric Oxide, pphm	1.1*	10.4	0.2	< 0.2
	Total Nitrogen Oxides, pphm	7.8*	30.2	1.0	< 0.4
	Oxidants, pphm	13	3	9	9

* at 1240 PST

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7. REFERENCES

1. "Gas Phase Titration of Atmospheric Ozone,"
J. J. Bufalini
Environmental Science and Technology 2, 703 (1968)

2. "Selected Methods for the Measurement of Air Pollutants,"
Interbranch Chemical Advisory Committee
U. S. Public Health Service Publication No. 999-AP-11, (1965)